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Organic Chemistry.

The Combustion of Methane to Formaldehyde. H. Tropsch and O. Roelen (*Brennstoff-Chem.*, 1924, **5**, 37—42).—A gas mixture containing methane and oxygen was passed through a quartz tube (without a catalyst), heated in an oven, and the formaldehyde produced absorbed in water and determined titrimetrically. The effect of varying the methane : oxygen ratio in the gas, the diameter of the tube, the reaction temperature, and the gas velocity through the tube, was studied. The yield of formaldehyde first increases with increasing gas velocity (the other factors being kept constant), reaches a maximum, and then decreases, a characteristic curve being obtained by plotting the results graphically. In the experiment in which the highest yield of formaldehyde was obtained the gas velocity was as high as 20 m. per sec. The tubes employed had cross-sectional areas of 63·5, 13·5, and 1·4 sq. mm., respectively, and the highest yields were obtained with the second of the three. If the oxygen content of the gas used is maintained constant (about 16—19%) and the methane content is varied, the highest concentration of formaldehyde in the resulting gas is obtained with a methane : oxygen ratio of 1 : 1, as required by theory. When working at high temperatures, the maximum is only obtained by starting with a high gas velocity and gradually diminishing it, much lower results being obtained by working conversely. With increasing reaction temperature, the absolute quantity of formaldehyde produced increases, but the yield per unit of methane decomposed diminishes. The highest yield of formaldehyde, viz., 5·96% of the methane treated, was obtained with a gas containing 1·2% of methane and 19·4% of oxygen, whilst a maximum yield of 70% of the methane decomposed was obtained at a reaction temperature of 700°, showing that formaldehyde is formed as the principal product in the action of oxygen on methane. Discrepancies between the present results and those of previous workers are discussed. W. T. K. B.

The Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Methane and Air. W. P. Jorissen and J. Velíšek (*Rec. trav. chim.*, 1924, **43**, 80—86).—The limits of inflammability of mixtures of methane and air are found to be 5·4% and 14·1% of methane. These limits are considerably modified by the presence of vapours of non-inflammable liquids. In presence of 0·7 to 0·8% of perchloroethylene, the limits are 7·35 and 10·15%; with 0·7 to 0·8% of tetrachloroethane, 7·15 and 9·15%; with 1% of pentachloroethane, 5·95 and 10·3%. In presence of 20% of dichloroethylene, 5% of trichloroethylene, or of 12·2% of carbon tetrachloride explosion is entirely inhibited, whilst with 8·5% of carbon tetrachloride the limits are 9·0 and 9·9% of methane. E. H. R.

The Cracking Process of Burton. H. I. WATERMAN and H. J. W. REUS (*Rec. trav. chim.*, 1924, **43**, 87—92).—It has been claimed that condensation under pressure in the oil-cracking process leads to the production of distillates free from unsaturated hydrocarbons. The authors are unable to verify this claim. [Cf. *B.*, 1924, 207.] E. H. R.

The Generation of Ethylene from Alcohol. T. HISAMURA and Y. IMAOKA (*Kwaken Hôkoku*, 1923, No. 7, 1—21).—Ethylene is prepared by passing alcohol vapour over "adsol" electrically heated at 390—400°, the yield being about 83%. (Adsol is a product used for drying air and is prepared from Japanese acid clay by pressing and burning; cf. Japan. Pat. 42368.) The rate of passing alcohol is 60—80 c.c. (in liquid) per hour, the thickness of the layer of the catalyst is 7 cm., and the resulting gas contains 98% of ethylene. After ten hours' passage of the vapour the yield decreases to 71%; the catalyst may, however, be re-activated by heating it for about thirty minutes at 650—700° in a current of air. K. K.

The Additive Power of Iodine with regard to Ethylenic Compounds. E. ANDRÉ (*Bull. Soc. chim.*, 1923, **33**, [iv], 1641—1647).—The author has studied the action of iodine in various solvents on olive, sesamé, poppy, and cod-liver oils, also on *iso*-heptene and phenylbutylene. The results obtained are compared with the iodine values furnished by Hanus' method, and show that the element itself is fairly active. Least activity is shown by the violet solutions in carbon tetrachloride and carbon disulphide; the brown solution in acetic acid and the violet-red chloroform solution exhibit much greater activity, the latter in some cases fixing 97% of the amount used in an iodine value determination. A second series of experiments, in which the iodine concentration was in each case $N/10$, gave similar results from the comparative point of view, although the ratio of iodine fixed to iodine value decreases considerably on dilution. The additive action in respect of ethylenic compounds seems to be capricious, as the same reactants under apparently similar conditions yielded discordant results in many cases. H. J. E.

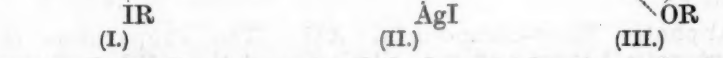
Aliphatic Nitro-compounds. XIV. The Preparation of Nitroacetic Esters and the Alkylation of their Silver Salts. W. STEINKOPF [and, in part, E. A. HAUGEN, A. SCHKADE, T. HÖPNER, and B. NOWY] (*Annalen*, 1923, **434**, 21—34).—Ethyl nitroacetate, b. p. 97°/13 mm., is prepared by passing dry hydrogen chloride into a solution of the acid, or a suspension of its potassium salt, in absolute alcohol at 0°, or by the gradual addition of concentrated sulphuric acid to a solution of the acid in alcohol at −15°. Its ammonium salt, long needles, has m. p. 124° (cf. Bouveault and Wahl, A., 1901, i, 4). The silver salt, if prepared from the pure ammonium salt, may be kept for a week before it becomes discoloured; it darkens at 40°, and decomposes at 117—119°. The following esters are similarly prepared: methyl, b. p. 106—110°/31 mm.; *propyl*, b. p. 105°/18 mm.; iso*propyl*, b. p. 92·2—

93·2°/12 mm. (*ammonium* salt, m. p. 107—109°); iso*butyl*, b. p. 111·5—112·5°/15 mm. (*ammonium* salt, m. p. 110—112°); iso*amyl*, b. p. 122—123°/16 mm. (*ammonium* salt, m. p. 112—115°).

The silver salt of ethyl nitroacetate (1 mol.) is gradually added to methyl iodide (2 mols.) at or below 0°. The product contains ethyl α-nitropropionate (cf. Steinkopf and Supan, A., 1911, i, 4) and *ethyl nitroacetate* aci*methyl ether*, $CO_2Et{\cdot}CH{:}NO_2Me$, a colourless liquid, b. p. 84°/2·5 mm., which gives a red coloration with ferric chloride, and is decomposed by means of concentrated hydrochloric acid at 70° into formaldehyde and *iso*nitrosoacetic acid. Similarly, the use of ethyl iodide leads to the formation of ethyl α-nitrobutyrate (cf. Schmidt and Widmann, A., 1909, i, 453) and *ethyl nitroacetate* aci*ethyl ether*, a colourless liquid, b. p. 81°/3 mm. These *aci*nitroethers, in which, in addition to the nitro group, there is only one other negative radical, are quite stable, and do not show any tendency to undergo isomerisation to the *C*-alkyl derivative. The view of Hantzsch and Voigt (A., 1912, i, 151), that two such radicals are necessary to stabilise an *aci*nitroether, is therefore incorrect.

It is probable that the compound, m. p. 114°, obtained by Ratz (A., 1906, i, 238) from silver nitroacetamide and ethyl iodide is an *aci*nitroether of the formula $CH_2ON{\cdot}CH{:}NO_2Et$.

During the action of methyl iodide on silver ethyl nitroacetate (above), the following phenomena are observed. If the salt is added at about −20°, it dissolves immediately to give a deep brown solution, the colour of which rapidly gives place to a white opalescence; silver iodide is then precipitated. If the addition is made at −60°, there is no reaction; as the mixture is allowed to become warm the solid is gradually dissolved, to give a colourless solution. This is stable over quite a wide range of temperature. Suddenly, however, the solution becomes dark. The brown colour then disappears as before, and silver iodide makes its appearance. It is supposed that in the colourless solution there is a molecular



(I.) (II.) (III.)

compound (I); the appearance of the brown coloration is due to a kind of double decomposition, resulting in the formation of a halochromic complex (II), from which the removal of silver iodide gives stereoisomeric *aci*nitroethers, $CO_2Et{\cdot}C(H){=}O{:}N{\cdot}OR$ and $CO_2Et{\cdot}C(H){=}RO{\cdot}N{:}O$. These are then stabilised, the former by isomerisation to the *C*-alkyl derivative, and the latter by " conjugation " (III) (Hantzsch and Voigt, *loc. cit.*).

iso*Propyl mercuri*aci*-nitroacetate anhydride*, $CO_2Pr^{\beta}{\cdot}C{:}\overset{NO}{\underset{Hg}{>}}O$, is obtained by the addition of concentrated mercuric chloride solution to an aqueous solution containing sodium acetate and the *aci*ammonium salt of *iso*propyl nitroacetate; the iso*butyl* and

iso*amyl* derivatives are prepared in a similar manner. These compounds resemble ethyl nitroacetate *aci*mercurianhydride (cf. Prager, A., 1913, i, 5); they are white solids, which sublime when heated, and are soluble in dilute sodium hydroxide solution, potassium cyanide solution, or hydrochloric acid. The solution in alkali does not react with potassium iodide. The action of mercuric chloride on potassium or ammonium nitroacetate gives, apparently, a heterogeneous product, which does not sublime on being heated, but decomposes violently.

Diammonium nitroacetate, $NH_4O{\cdot}CO{\cdot}CH{:}NO_2{\cdot}NH_4$, a white solid, is obtained from ammonia and nitroacetic acid in dry ethereal solution; the *disilver* salt is also prepared.

Condensation could not be effected between ethyl nitroacetate and benzaldehyde, piperonal, or anisaldehyde, using methylamine, ethylamine, amylamine, or piperidine as catalysts. W. S. N.

The Formation of Ethyl Chloride from Ethylene and Hydrogen Chloride. E. Berl and J. Bitter (*Ber.*, 1924, **57**, [*B*], 95—99).—The union of ethylene with hydrogen chloride in the presence of aluminium chloride is effected most advantageously at 130—170°, but the slowness of the reaction renders prolonged contact with the catalyst necessary for the production of good yields of ethyl chloride; the latter substance is absorbed from the products of the reaction by active charcoal.

Ethyl chloride is analysed by passing it through a very narrow quartz tube heated at 900°, absorption of the hydrogen chloride by sodium hydroxide, and titration of the chloride by *N*/10-silver nitrate. The process is applicable to dichloroethylene, but not to chloroform or benzyl chloride. H. W.

Chlorination of Carbon Chains. Chlorination of Normal Butyl Alcohol. H. Gault and R. Guillemet (*Bull. Soc. chim.*, 1923, **33**, [iv], 1792—1801).—The chlorination, at definite temperatures in diffused daylight, of *n*-butyl alcohol has been studied, using iron (steel wire) as a catalyst, and different methods of procedure, viz., either bubbling chlorine through the alcohol, or (counter-current method) allowing the latter to run in a helical path down a vertical tube up which the chlorine passed. A comparative chlorination was carried out, in each case, in absence of the catalyst. The latter does not affect the yield of main product, but diminishes the amounts of by-products. These are produced in larger amount in cold than in hot chlorinations, owing to the formation of acetals in the latter case, and resulting restriction of action.

Chlorination, at temperatures not higher than 10°, by the bubbling method, gave, in presence of iron, a single product (corresponding with 18—20% of the alcohol used), shown to be the *dibutyl acetal* of a *chlorobutaldehyde*, $C_4H_7Cl(OBu)_2$, a colourless liquid, b. p. 125°/15 mm. The latter in presence of hydrogen chloride in a closed tube at 120—130° was partly converted into an unstable *liquid* (b. p. 80—90°/15 mm., with loss of hydrogen

chloride) which reduced Fehling's solution and was converted by alcoholic hydrogen chloride into an *acetal*, $CHMeCl{\cdot}CH_2{\cdot}CH(OEt)_2$(?).

Chlorination by the bubbling method (using the catalyst) at 40—80° gave the *dibutyl acetal* of a *dichlorobutaldehyde* (yield, 50% of alcohol taken; b. p. 140—142°/15 mm.). This acetal, although unaffected by diluted mineral acids at the ordinary pressure, was partly converted, on heating at 125° in presence of hydrogen chloride, into a *liquid* (b. p. 105—110°/15 mm.) which reduced Fehling's solution, and lost hydrogen chloride on being distilled. The acetal, on being heated with acetic anhydride in a closed tube at 200°, was partly converted into *n*-butyl acetate and a *dichlorobutylidene diacetate* (b. p. 124—129°/15 mm.) (?), and with chromic acid yielded butyric acid and a *butyl dichlorobutyrate* (b. p. 210—215°).

The counter-current method gives less homogeneous products than are given by the bubbling method. E. E. T.

Oleic Alcohol. Y. Toyama (*Chem. Umschau*, 1924, **31**, 13—16; cf. A., 1922, i, 895).—The acetyl ester of the oleic alcohol obtained from rabukazame oil gave on oxidation with potassium permanganate nonylic acid and acetylhydroxynonylic acid. This result, coupled with the previously established fact that the same substance gives the acetyl ester of normal octadecyl alcohol on hydrogenation, establishes the formula, $CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CH_2{\cdot}OH$, for oleic alcohol. It is accordingly identical with the alcohol obtained from ethyl oleate. It has d_4^{15} 0·8523, d_4^{20} 0·8491, d_4^{40} 0·8367; n_D^{15} 1·4626, n_D^{20} 1·4607, n_D^{40} 1·4530, b. p. 333—335°/760 mm., 197°/10 mm., 209°/15 mm., 228°/30 mm. Elaidic alcohol has m. p. 35·0—35·5°, d_4^{40} 0·8338, n_D^{40} 1·4522, b. p. about 333°/760 mm., 198°/10 mm., 210°/15 mm., 229—230°/30 mm. These two isomeric alcohols are very stable and show no tendency to change into one another on heating or acetylation. They are sharply differentiated from one another by their melting points. H. C. R.

Equilibria between some Glycols and their Acetone Compounds. J. Böeseken and P. H. Hermans (*Rec. trav. chim.*, 1923, **42**, 1104—1110).—The authors have prepared the acetone derivatives [*iso*propylidene ethers] of ethylene glycol, propane-αβ-diol, propane-αγ-diol, glycerol, and monochlorohydrin, 1 : 3-*ciscyclo*pentanediol, and 1 : 2-*ciscyclo*hexanediol. The method of preparation used was to heat suitable quantities of the glycol and acetone with sulphuric acid. The following new physical data are recorded: *iso*propylidene ether of ethyleneglycol, b. p. 92·5—92·7°, d_4^{17} 0·9469, n_D^{17} 1·40024, solubility in water, 1 vol. in 3½—4 vols. at 18°; *iso*propylidene ether of propane-αβ-diol, b. p. 98—99°, $n_D^{18·5}$ 1·40191, $d_4^{18·5}$ 0·9090, solubility in water, 1 vol. in 9—10 vols.; *iso*propylidene ether of propane-αγ-diol, b. p. 123—125°, $n_D^{18·5}$ 1·4252, $d_4^{16·5}$ 0·9587; *iso*propylidene ether of α-monochlorohydrin, b. p. 116°/11 mm., $d_4^{17·5}$ 1·322, $n_D^{17·5}$ 1·4820. The molecular weight of these compounds has been determined and is found to show no association of the molecules. The equilibrium constants of the reaction, acetone+

diol $\rightleftharpoons$ *iso*propylidene ether+water, have been ascertained in each case, and the values compared with the difference in electrical conductivity of a 0·5 mol. solution of the diol containing 0·5 mol. of boric acid, and the sum of the electrical conductivities of a 0·5 mol. solution of boric acid and a 0·5 mol. solution of the diol. The two sets of figures are parallel, which is taken to indicate that the glycols combine with the same facility with acetone as they do with boric acid. A modification of the Le Bel–Henniger fractionating column was used in the purification of the materials, the bulbs of the original apparatus being connected with capillary tubes instead of the one opening; this causes the outside lateral tubes continuously to contain liquid. J. F. S.

The Condensation of Mannitol with Olive Oil. J. C. Irvine and H. S. Gilchrist (*J. Chem. Soc.*, 1924, **125**, 10—15).—"Mannitol fat" (cf. Lapworth and Pearson, A., 1919, i, 570), prepared by the interaction of mannitol and olive oil in the presence of sodium ethoxide, consists essentially of *mannitan dioleate*, which is formed by the dehydration of *mannitol dioleate*, the first product of the reaction. Further dehydration (at 200° under reduced pressure) results in the formation of iso*mannide dioleate*. Treatment of mannitan dioleate with excess of methyl iodide and silver oxide results only in the formation of *monomethylmannitan dioleate*, together with a trace of *monomethyl*iso*mannide* (n_D 1·4506), from *iso*mannide originally present. On boiling with 0·5% alcoholic hydrogen chloride, monomethylmannitan dioleate gives ethyl oleate and *monomethylmannitan*, a viscous syrup. The latter was methylated to *trimethylmannitan*, a clear, mobile syrup, b. p. 115—120°/0·18 mm., n_D 1·4518. Structural considerations based on the reactions described lead to the formula

$$CH_2{\cdot}CHOX{\cdot}CHOX{\cdot}CH{\cdot}CHOH{\cdot}CH_2OH,$$
$$\llcorner\!\!-\!\!-\!\!-\!\!-O\!\!-\!\!-\!\!-\!\!-\lrcorner$$

where X is the oleyl residue, for "mannitol fat." No more than two acyl groups can be introduced into the mannitol molecule. F. G. W.

The αγ-Dichloropropyl Ethers and the Corresponding Acetals. W. Dulière (*Bull. Soc. chim.*, 1923, **33**, [iv], 1647—1654; cf. Wohl, A., 1898, i, 555).—The ethers were prepared by saturating an equimolecular mixture of acraldehyde and aliphatic alcohol with dry hydrogen chloride at −10°, the products being purified by distillation under reduced pressure. They are colourless liquids of characteristic odour, decomposing with liberation of hydrogen chloride when heated at atmospheric pressure. They are not miscible with water, but react with it, hydrogen chloride being formed. With aliphatic alcohols, particularly those containing few carbon atoms, they readily produce acetals by reaction with the α-chlorine atom, and with magnesium alkyl halides monochloroethers are obtained. The following are described: *methyl αγ-dichloropropyl ether*, b. p. 45°/12 mm., d^{20} 1·187, n_D^{20} 1·44777, yielding, with methyl alcohol, the acetal *γ-chloro-αα-dimethoxy-*

propane, b. p. 45°/12 mm., d^{20} 1·059, n_D^{20} 1·41631; *ethyl αγ-dichloropropyl ether* has b. p. 56°/12 mm., d^{20} 1·122, n^{20} 1·44235, and γ-chloro-α-diethoxypropane has d^{20} 0·991 (cf. Wohl, *loc. cit.*); *propyl αγ-dichloropropyl ether*, b. p. 65°/12 mm., d^{20} 1·100, n_D^{20} 1·44576, and *γ-chloro-αα-dipropoxypropane* has b. p. 87°/20 mm., d^{20} 0·972, n_D^{20} 1·42871; *αγ-dichloropropyl* iso*butyl ether*, b. p. 89°/21 mm., d^{20} 1·067, n_D^{20} 1·44305, and *γ-chloro-α-di*iso*butoxypropane*, b. p. 105°/12 mm., d^{20} 0·936; *αγ-dipropyl* iso*amyl ether*, b. p. 103°/20 mm., d^{20} 1·027, turns brown and decomposes on being kept.

H. J. E.

The Alkyl Titanates. F. Bischoff and H. Adkins (*J. Amer. Chem. Soc.*, 1924, **46**, 256—259).—*Tetramethyl titanate*, prepared from methyl alcohol, sodium, and titanium tetrachloride, crystallising point 209—210°, b. p. 243°(corr.)/52 mm., is rapidly hydrolysed in air. *Tetraethyl titanate*, prepared similarly from ethyl alcohol, had b. p. 205°/156 mm., 145°/8·5 mm., d_{20}^{20} 1·107. *Tetra*-iso*propyl titanate*, obtained mixed with 4% of *iso*propyl alcohol as a constant-boiling mixture, has b. p. 230°/740 mm. *Tetra*-n-*butyl titanate* has b. p. 185—187°/16 mm., d_{20}^{20} 0·993. On boiling the higher esters with methyl alcohol, a quantitative yield of the tetramethyl derivative is obtained. All these esters are colourless.

F. A. M.

Octyl Mercaptan. H. Kahn (*Bul. Soc. Chim. România*, 1923, **5**, 70—72).—Pure octane, obtained by the repeated fractionation of benzene from Ploesti and removal of aromatic hydrocarbons by repeated action of a mixture of nitric and sulphuric acids, is converted into octyl chloride, which, when treated with a saturated alcoholic solution of potassium hydrogen sulphide, yields *octyl mercaptan*, a colourless liquid of disagreeable odour, b. p. 198—200°. When heated, it readily decomposes into octyl sulphide and hydrogen sulphide.

J. W. B.

Valeric Acid. S. Koizumi and H. Ichinose (Japan. Pat. 41910).—Valeric acid is prepared from amyl alcohol by electrolytic oxidation in 5—20% sulphuric acid solution at the ordinary temperature. Lead or lead peroxide is used as anode, and platinum, copper, iron, or nickel as cathode, without diaphragm. The addition of 1 g. of oxides of vanadium, chromium, or manganese to 1 litre of the sulphuric acid promotes the reaction. The electrolyte is vigorously agitated during the operation, the current density being 1—5 amp. per sq. dm. The product separates in a nearly pure state, the current yield being above 80%.

K. K.

Palmitic and Stearic Anhydrides. D. Holde, J. Ripper, and F. Zadek (*Ber.*, 1924, **57**, [*B*], 103—104).—Since the constants recorded in the literature for these substances are very discordant, they have been redetermined with material prepared by Albitzky's method as modified by Holde and Tacke (A., 1920, i, 811). Palmitic anhydride has m. p. 64°, d_4^{83} 0·8383, whence d^{15} 0·8832, and n^{100} 1·4679. Stearic anhydride has m. p. 72°, d_4^{80} 0·855, whence d_4 0·897, and n_D^{100} 1·4284.

H. W.

The Composition and Constitution of Elæostearic Acid. L. MAQUENNE (*Bull. Soc. chim.*, 1923, **33**, [iv], 1654—1655).—The author claims priority over Vercruysse (A., 1923, i, 533) and refers to his own work (A., 1903, i, 62) in support of his view that the extreme readiness with which the acid undergoes oxidation has led to errors with regard to its formula and m. p., which are $C_{18}H_{30}O_2$ and 48°, respectively. H. J. E.

Elaidic Acid and its Anhydride. D. HOLDE and K. RIETZ (*Ber.*, 1924, **57**, [*B*], 99—102).—Elaidic acid, obtained by the action of nitrous acid on oleic acid, crystallises in colourless, lustrous leaflets, m. p. 44·4° (corr.), n_D^{100} 1·4308. Elaidic anhydride, prepared from the acid and acetic anhydride, has m. p. 46·4° (corr.), d_{15}^{82} 0·8476, d_{15}^{93} 0·8396, d_4^{100} 0·8338, n_D^{100} 1·4339.

The electrolytic conductivities of oleic and elaidic acids and their anhydrides in very highly purified acetone have been measured. Little differences are observed between the constants of the acids and their anhydrides, but those of elaidic acid and its anhydrides are somewhat higher than those of the oleic compounds. H. W.

The Relative Solubilities of the Calcium and Magnesium Salts of the Higher Fatty Acids. W. BILTZ and W. RÖHRS (*Z. angew. Chem.*, 1923, **36**, 609—611).—A study of the equilibria resulting from the action of solutions of calcium chloride on solid magnesium stearate and oleate. The mixture was heated for one hour, cooled, and filtered, the extent of double decomposition being found from analysis of the filtrate. When equimolecular proportions were used, the amounts of calcium stearate and oleate produced were 88% and 81%, respectively; these values increased to 98% and 90% on doubling the molecular ratio of calcium chloride. Fractional precipitation of a mixture of equivalent quantities of calcium and magnesium chlorides with potassium stearate and oleate yielded mainly calcium salt (Ca 6·54%, Mg 0·03%). Experiments on commercial soap are also described. The general conclusion is drawn that calcium stearate is considerably and calcium oleate appreciably less soluble than the corresponding magnesium salts. H. J. E.

The Composition of Whale Oil. C. H. MILLIGAN, C. A. KNUTH, and A. S. RICHARDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 157—166).—Whale oil is shown to contain a complicated mixture of fatty acids having 14 to 22 carbon atoms, probably with a small amount of C_{24} acids. The highly unsaturated acids are chiefly those containing 20 and 22 carbon atoms. The percentage composition of the mixture of fatty acids is approximately: (C_{14}) myristic 4·5; (C_{16}) palmitic 11·5, palmitoleic 17·0; (C_{18}) stearic 2·5, unsaturated (nearly all oleic) 36·5; (C_{20}) unsaturated 16; (C_{22}) unsaturated 10; (C_{24}) unsaturated 1·5; unsaponifiable 0·7. F. A. M.

The Catalytic Hydrogenation of some Unsaturated Compounds, especially Oils, by Means of Nickel at the Ordinary Temperature. M. TANAKA (*Chem.-Ztg.*, 1924, **48**, 25—26).—The

author has extended the work of Kelber (A., 1916, ii, 309, 609) by using nickel, precipitated on kieselguhr, for reduction at the ordinary temperature of ethyl cinnamate, cinnamaldehyde, cinnamyl alcohol, azoxybenzene (to azobenzene, hydrazobenzene, and aniline), ricinostearol di-iodide, perilla oil, hemp-seed oil, chrysalis oil, and shark oil. Details of the amounts of hydrogen fixed are given and also of similar experiments carried out with a palladium catalyst for comparison. [Cf. *B.*, Mar.] H. J. E.

Reaction of Zinc on Mixtures of Ethyl α-Bromo*iso*butyrate and Aldehydes or Ketones. I. Coucoulesco (*Bul. Soc. Chim. România*, 1923, **5**, 63—70).—The action of zinc on mixtures of ethyl α-bromo*iso*butyrate with *iso*valeraldehyde, *iso*propyl ketone, and acetophenone, respectively, has been studied. With *iso*valeraldehyde, the reaction takes the normal course and yields *ethyl β-hydroxy-ααδ-trimethylhexoate* (b. p. 173—175°/140—145 mm.), which is hydrolysed to *β-hydroxy-ααδ-trimethylhexoic acid*, colourless tetragonal or hexagonal crystals, m. p. 81°, α=0·00147. The acid is soluble in alcohol and in ether. The *barium*, *silver*, *potassium*, *zinc*, and *lead* salts are described. The action either of dilute sulphuric acid (1 : 10) or of hydrogen iodide on this acid yields the *γ-lactone*, $CHMe_2{\cdot}CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO$, b. p. 221—222°/742 mm., probably owing to the initial formation of the βγ-unsaturated acid. Oxidation of the acid with potassium permanganate yields only unchanged material, carbon dioxide, and water.

With the two ketones, the main products isolated are ethyl *iso*butyrate, unchanged ketones, and a small quantity of oil, which is probably the expected ester of the hydroxy-acid. This on hydrolysis yielded an acid oil from which a pure substance could not be isolated. J. W. B.

Synthesis of the Higher Monoalkylmalonic Acids. (Mrs.) G. M. Robinson (*J. Chem. Soc.*, 1924, **125**, 226—231).—A method for the preparation of higher monoalkylmalonic acids, suitable for use with considerable quantities of material in one operation, and in which the formation of the corresponding dialkyl acids is minimal, is as follows. A mixture of the higher alkyl iodide (1 mol.), ethyl cyanoacetate (2 mols. or more), and potassium carbonate (1·5 mols.) is boiled under a reflux condenser and at a reduced pressure until the reaction is completed. The unchanged cyanoacetate is then recovered by distillation, the whole residue hydrolysed with hot 20% sodium hydroxide, and the product precipitated with dilute sulphuric acid. Under these conditions, the hydrolysis of α-cyano*cyclo*hexylacetic acid yielded only the malonamic acid, $CH_2<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>CH{\cdot}CH(CO{\cdot}NH_2){\cdot}CO_2H$, a result ascribed to steric hindrance. The remaining cyanoacetic acids examined were completely hydrolysed to the corresponding malonic acids. *cyclo-Hexylmalonamic acid*, colourless needles, m. p. 184°, was unattacked on heating for four hours with alcoholic potassium hydroxide.

*k**

Heated in a tube, it loses carbon dioxide and forms *cyclo*hexylacetamide.

The preparation of *n*-heptylmalonic acid, *n*-octylmalonic acid, rhombic prisms, m. p. 115°, n-*undecylmalonic acid*, rectangular needles, m. p. 108°, and *n*-hexadecylmalonic acid, m. p. 119°, is described in detail.

n-*Decyldimethylcarbinol*, obtained from methyl undecoate and magnesium methyl iodide, is a mobile liquid, b. p. 145°/10 mm.

F. G. W.

The Chlorosulphides of Carbon. Decomposition in Presence of Iron. M. Delépine and J. Giron (*Bull. Soc. chim.*, 1923, **33**, [iv], 1785—1792).—The chlorosulphides of carbon, when left in contact with metallic iron, are converted into sulphur and carbon tetrachloride. The action is catalytic, the iron suffering very little alteration. The chlorosulphides examined were: thiocarbonyl chloride, perchloromethyl mercaptan (also examined in presence of carbon disulphide and/or sulphur chloride), and the chlorosulphides represented by the formulæ: (1) $CCl_3 \cdot S \cdot CS \cdot Cl$, (2) $CCl_3 \cdot S_3 \cdot CCl_3$, and (3) $C_2Cl_6S_4$ (obtained from the residue in the distillation of perchloromethyl mercaptan, and having b. p. 150—154°/26 mm.). E. E. T.

Condensation of Citral with Ketones and Synthesis of some New Ionones. H. Hibbert and L. T. Cannon (*J. Amer. Chem. Soc.*, 1924, **46**, 119—129).—Citral, purified by a modification of Tiemann's method (A., 1899, i, 622), was condensed with acetone by means of sodium ethoxide, giving a 55% yield of pure ψ-ionone. The best condensing agent for converting ψ-ionone into α-ionone was found to be 85% phosphoric acid. *ψ-Ethylionone*, prepared from citral and methyl propyl ketone, is a pale yellow oil, b. p. 155—158°/8 mm.; its structure is probably $Me_2C{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot CH{:}CH \cdot CO \cdot Pr$. It is converted by means of 85% phosphoric acid into *ethylionone*, a pale yellow oil, b. p. 138—140°/8 mm., possessing a pleasant odour of violets.

Citral condenses with acetophenone, in presence of sodium ethoxide, to form *phenyl-ψ-ionone*, an odourless, viscous, pale yellow oil, b. p. 182—185°/4 mm. *Phenylionone*, prepared from it by the action of 85% phosphoric acid, is a pale yellow, viscous oil, b. p. 172—175°/4·5 mm., with a very faint but rather disagreeable odour, the violet fragrance being almost entirely suppressed.

Attempts to condense citral with diethyl ketone or dipropyl ketone were unsuccessful. F. A. M.

Ring-chain Tautomerism. IX. The Mutarotation of the Sugars. J. W. Baker, C. K. Ingold, and J. F. Thorpe (*J. Chem. Soc.*, 1924, **125**, 268—291).—A proof, from a dynamical investigation and survey of structural evidence, supported by data from two series of crucial experiments, that the mutarotation of the sugars is a case of ring-chain tautomerism in the sense

$$[H]O \cdot (C)_n \cdot \overset{|}{C}{:}O \rightleftharpoons \overset{\boxed{}}{O \cdot (C)_n \cdot C} \cdot O[H]$$

on lines suggested by Jacobson and Stelzner (Meyer and Jacobson's "Organischen Chemie," 2 Aufl., 1, **2**, 886, 910, 915, 927), and not dependent on the intermediate formation of hydrates as suggested by Lowry (T., 1903, **83**, 1316) and Armstrong (T., 1903, **83**, 1309). It is postulated that the phenomenon is of the same nature in all cases and not of varying kinds as suggested by Irvine and Steele (T., 1915, **107**, 1239—1240). The full mathematical derivation of the form and spacing of the mutarotation–time curves on the mutarotation–time–concentration diagram, according to the tautomeric-hydrogen theory, is given. It is deduced that whilst the form of the mutarotation–time curves can be accommodated by the intermediate-hydrate theory, the spacing of curves obtained from measurements of mutarotation in presence of varying initial concentrations of water is zero, in direct contradiction of the consequences of the hydrate theory, and in agreement with the experimental results. From structural considerations, it is pointed out that whilst *d*-fructose should not be capable of mutarotation according to Armstrong's theory, its mutarotation has actually been measured in water, pyridine, and formamide solutions, and that *d*-glucoseoxime, *d*-glucoseanilide, *d*-glucoseimine, *d*-glucosephenylhydrazone, and ethylamino-*d*-glucose, all show mutarotation contrary to expectations based on Lowry's views. Also, no substance which, according to all three theories, should be incapable of mutarotation, has been found to exhibit this phenomenon, although interconversion of isomeric forms can sometimes be effected by reagents. This is shown to be at variance with Armstrong's views, and it is suggested that the mechanism of such conversions is fundamentally different from that of mutarotation. Experimentally, the mutarotation of tetra-acetyl-*d*-glucose in ethyl acetate solution at 44·8° was measured under conditions such that water was rigorously excluded, or present in small, accurately known concentrations of 0·025, 0·05, and 0·1%, respectively, these amounts being small in proportion to that possibly present in the dried materials. The velocity constants were, respectively, 0·0222, 0·0221, 0·0209, and 0·0208, *i.e.*, independent of the small initial concentration of water. The mutarotation of α-*d*-glucose in methyl alcohol was also measured at the same temperature, first with dried materials, and then in presence of 0·5, 1·0, and 2·0%, respectively, of added water, these concentrations of water being relatively large in comparison with that which might have been present originally. The initial velocities were, respectively, 0·165, 0·178, 0·246, and 0·379. These values are not in proportion to the initial concentration of the water, as the hydrate theory demands. F. G. W.

Oxidation of Dextrose by Iodine in the Presence of Insulin. G. A. Alles and H. M. Winegarden (*J. Biol. Chem.*, 1923, **58**, 225—234).—The rate of oxidation of dextrose by iodine is not altered by the presence either of insulin alone or of insulin plus liver extract, blood-serum, or oxalated blood. Since the rates of oxidation of the various sugars differ greatly, it is evident that, under the conditions employed, insulin does not transform dextrose

into a more reactive form (cf. Winter and Smith, A., 1923, i, 513). E. S.

A Quantitative Study of the Interaction of Dextrose and Phenylhydrazine. E. KNECHT and F. P. THOMPSON (*J. Chem. Soc.*, 1924, **125**, 222—226).—In view of the strong reducing properties of phenylhydrazine and its resistance to reduction by titanous chloride, the reaction between phenylhydrazine and dextrose was studied to confirm quantitatively the formation of aniline and ammonia simultaneously with the osazone, and to discover the fate of the reactants in view of the low yields of osazone usually obtained. Pure dextrose (1 mol. : 3·6 g.) and phenylhydrazine (3 mols. : 6·48 g.) were dissolved in a mixture of water (190 c.c.) and glacial acetic acid (10 c.c.) and heated for three hours on the water-bath. A parallel experiment was made using *p*-nitrophenylhydrazine, but at twice the dilution of dextrose and phenylhydrazine. The osazone was filtered off and weighed. The unchanged phenylhydrazine was determined by boiling with Fehling's solution and measuring the nitrogen evolved, and the ammonia by a distillation during which tarring was avoided. The amount of ammonia produced in both cases was in agreement with that calculated from the weight of osazone obtained, in accordance with Fischer's equation, but it is inferred that a portion of the dextrose remains in solution as phenylhydrazone. The addition of aniline acetate or ammonium acetate to the reaction mixture increases the yield of osazone. By heating 3·6 g. of dextrose and 6·48 g. of phenylhydrazine with 20 c.c. of glacial acetic acid diluted to 100 c.c. with water, for three hours at water-bath temperature, a yield of osazone corresponding with 84% of the theoretical may be obtained. F. G. W.

A Synthetic Fat containing a Methylglucoside Residue. J. C. IRVINE and H. S. GILCHRIST (*J. Chem. Soc.*, 1924, **125**, 1—10).—When olive oil (1 mol.) is heated with α-methylglucoside (3 mols.) in presence of sodium ethoxide at 140°, *methylglucoside mono-oleate* is formed, and this on further heating at 220°/12 mm. loses water and forms *anhydro-methylglucoside mono-oleate*, a viscous, yellow oil, $[\alpha]_D^{15} + 38°$ in chloroform. Attempts to introduce more than one oleyl residue failed. Treatment of the anhydro-monooleate with methyl iodide and silver oxide gave *monomethyl-anhydro-methylglucoside mono-oleate*, a mobile, yellow oil; this on boiling with methyl-alcoholic hydrogen chloride gave methyl oleate and *monomethyl-anhydro-methylglucoside*, a colourless, viscous syrup. The latter was further methylated to *dimethyl-anhydro-methylglucoside*, b. p. 115—120°/0·2 mm., n_D 1·4419, and hydrolysed with barium hydroxide to *monomethyl methylglucoside*, a colourless, viscous syrup. Further hydrolysis with 5% hydrochloric acid at 100° gave a syrupy monomethylglucose. Consideration of the reactions described leads to the formula,

$$\begin{array}{l} \text{CHOMe·CHOH·CHOX·CH·CH·CH}_2, \\ \quad\quad\quad\

Fluoroacetyl Derivatives of Sugars. II. Optical Rotation and Atomic Dimension. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1923, **45**, 2381—2390).—In comparing the optical rotations of monohalogen-acetyl derivatives of dextrose, cellose, xylose, and lævulose, the differences F–Cl, Cl–Br, Br–I are found to be approximately proportional to the differences in atomic diameter. This simple relation holds for the specific, but not for the molecular rotation. *Fluorotetra-acetyl-lævulose* is obtained from β-penta-acetyl-lævulose. It is readily soluble in chloroform, and has m. p. 112°, $[\alpha]_D^{20}$ −90·43° in chloroform. It is stable, colourless, and odourless. *Bromotetra-acetyl-lævulose* was prepared by the action of a solution of hydrogen bromide in glacial acetic acid on a solution of β-penta-acetyl-lævulose in the same solvent. It is a very unstable, crystalline solid, $[\alpha]_D^{20}$ −189·1° in chloroform, m. p. 65°. When preserved, it is transformed into β-tetra-acetyl-lævulose. F. G. P.

Unsaturated Reduction Products of the Sugars and their Transformations. VIII. M. BERGMANN [and, in part, H. SCHOTTE, E. RENNERT, S. LUDEWIG, and M. KOBEL] (*Annalen*, 1923, **434**, 79—110).—Fischer and Curme (A., 1914, i, 931) obtained a substance, which they described as lactal, by the hydrolysis of hexa-acetyl-lactal by means of barium hydroxide. This product had 1 mol. of water of crystallisation, $[\alpha]_D$ +26·77° to +26·95°, m. p. 184—186°, or, when anhydrous, m. p. 165—170°. Lactal prepared by using methyl-alcoholic ammonia instead of barium hydroxide is anhydrous, and has $[\alpha]_D^{16}$ +27·66° to +27·67°, m. p. 192° (corr.), decomp. about 212°. A sample so prepared is not changed on standing with barium hydroxide solution at 37° for two or three days. Lactal prepared by means of ammonia is reconverted by the action of acetic anhydride and pyridine into the hexa-acetate, m. p. 114°, but the product from "barytalactal" has m. p. 108—109°. It is thought that Fischer and Curme's material was simply impure lactal.

When lactal is boiled with water, the product has m. p. 198° (corr.), $[\alpha]_D^{17}$ +36·43°, but the other properties are, in general, unchanged.

Hexa-acetyl-lactal is converted by boiling with water into *ψ-lactal penta-acetate*, a heavy, snow-white powder (flat tablets, small, thin prisms, or elongated, hexagonal crystals), m. p. 123—124° (corr.) after previously softening, decomp. 190°. The structure of this compound is different from that of lactal or its hexa-acetate, because on treatment with acetic anhydride and pyridine it gives *ψ-lactal hexa-acetate*, aggregated prisms or needles, m. p. 127—128° (corr.), $[\alpha]_D^{18}$ +32·24°, which is reconverted, by boiling with water, into the penta-acetate. Both the penta- and the hexa-acetate of ψ-lactal have a bitter taste; the hexa-acetate does not give the pine-shaving reaction, and does not react with bromine, but it reduces ammoniacal silver nitrate solution, and gradually gives a red coloration with magenta–sulphurous acid. In its sensitiveness to even dilute mineral acids it resembles lactal and the deoxy-sugars.

When ψ-lactal penta-acetate is treated successively with cold methyl-alcoholic hydrogen chloride, sodium hydroxide solution (with cooling), and sodium hydroxide and methyl sulphate, a yellow syrup is obtained, b. p. 178—180°/0·3—0·4 mm., $n_D^{50\cdot5}$ 1·4661; this is the *pentamethyl* ether of a *compound*, $C_{12}H_{20}O_9$, isomeric with lactal. This series of reactions may involve a change of structure. When ψ-lactal penta-acetate is treated at 0° with a saturated solution of hydrogen bromide in glacial acetic acid, two molecular proportions of hydrogen bromide are taken up, giving a *dibromide*, $C_{22}H_{30}O_{13}Br_2$, small prisms or needles, m. p. 124° (corr.) (decomp.), $[\alpha]_D^{23}$ +69·6°. The latter is converted by means of silver carbonate in moist acetone solution into a *hydroxybromide*, $C_{22}H_{30}O_{13}Br(OH),\frac{1}{2}H_2O$, snow-white, glistening flakes, m. p. 87—88° after sintering at 80°, decomp. 110°. In dry methyl-alcoholic solution, the product is the corresponding *methoxybromide*, m. p. 147—148° (corr.), with subsequent decomposition, which is hydrolysed by means of methyl-alcoholic ammonia to the free *bromomethoxy*-derivative, snow-white, aggregated needles, m. p. 119° (decomp.). ψ-Lactal penta-acetate, which need not be isolated, is converted by the action of cold barium hydroxide solution into *iso*lactal, short, slender needles, which is very difficult to purify. It has a vigorous reducing action on Fehling's solution, and gives a green coloration with a pine shaving. With warm alkali, it becomes yellow or brown, whilst concentrated mineral acids give a red solution; it is not attacked by perbenzoic acid. *iso*Lactal has a slightly sweet taste, resembling that of lactose. The action of acetic anhydride and pyridine on *iso*lactal gives *iso*lactal *hexa-acetate*, rhombic prisms, or leaflets, m. p. 166—167° after sintering at 163°, $[\alpha]_D^{23}$ +55·30°, which gives the pine-shaving test, and has an insipid taste. By the action of boiling water, one acetyl group is eliminated. *iso*Lactal may be acetalised by means of methyl-alcoholic hydrogen chloride, or methylated by means of methyl sulphate; it is rapidly oxidised by means of aqueous bromine.

The action of perbenzoic acid, in warm ethyl acetate solution, on an aqueous solution of lactal gives *5-galactosidomannose*, needles, m. p. 196—197° (corr.), after slight softening. This compound has, initially, $[\alpha]_D^{25}$ +23° (about), rising to +30° after eighty minutes. It reduces Fehling's solution immediately, and reacts gradually with ammoniacal silver nitrate solution or magenta and sulphurous acid. With phenylhydrazine, it gives lactosazone; it is decomposed by emulsin.

The diacetate, obtained by boiling triacetylglucal with water, is converted by heating with acetic anhydride and sodium acetate at 100° into *ψ-glucal triacetate*, a colourless liquid, b. p. 150—165°/0·2—0·3 mm., which has a bitter taste and a pungent odour. It is reconverted by the action of boiling water into the diacetate, which is described as ψ-glucal diacetate. The triacetate is highly sensitive to the action of acids, and immediately becomes brownish-black when treated with cold alkali. It gives an intensely green

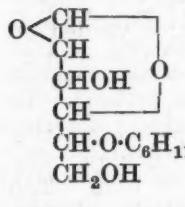
coloration with a pine shaving, and reacts with magenta–sulphurous acid, Fehling's solution, or ammoniacal silver nitrate. With bromine in chloroform solution at 18°, two atoms of halogen are absorbed, one of which may then be removed by boiling with silver carbonate and dry methyl alcohol. The action of 1% methyl-alcoholic hydrogen chloride on ψ-glucal diacetate gives a pale yellow syrup, from which the following fractions are isolated. (1) A colourless, mobile liquid, b. p. 68—69°/0·3 mm., n_D^{20} 1·4763, $[\alpha]_D^{22}$ +1·2°, apparently $C_7H_{10}O_3$, and perhaps the methyl*cyclo*acetal of a hydroxyaldehyde, with two bonds, and a methylene group adjacent to the acetalised aldehyde group. (2) A viscous, slightly yellow oil, b. p. 88—90°/0·1 mm., n_D^{20} 1·4984, $[\alpha]_D^{20}$ +15·50—+16·1°, evidently $C_8H_{12}O_4$. (3) A viscous, colourless liquid, apparently $C_7H_{12}O_4$, b. p. 120—121°/0·2 mm., n_D^{20} 1·4860, $[\alpha]_D^{20}$ +71·7—+72·2°. Each of these fractions gives a green pine-shaving reaction, and is sensitive to acids; Fehling's solution is not reduced. The action of cold barium hydroxide solution on ψ-glucal diacetate gives iso*glucal*, a syrup, b. p. 120—130°/0·2—0·3 mm. (but sublimes at about 60° at this pressure), $[\alpha]_D^{22}$ +43·15°, which is isolated as its *phenylbenzylhydrazone*, microscopic needles, m. p. 121—122°, $[\alpha]_D^{22}$ −22·38°, from which it is regenerated by boiling with aqueous benzaldehyde or concentrated formaldehyde solution, the former being preferable. *iso*Glucal is readily decomposed by means of acids or of alkali. It gives a very pronounced green coloration with a pine shaving, and vigorously reduces Fehling's solution. On keeping the syrupy material in a vacuum, *crystals* are gradually deposited, m. p. 49—50°, $[\alpha]_D^{18}$ +45·6°, which, in contrast with the original material, do not give a coloration with magenta–sulphurous acid. The syrupy *iso*glucal rapidly reacts with bromine, but in chloroform solution the reaction is apparently incomplete. Neutral or alkaline permanganate solution is immediately decolorised, but perbenzoic acid is not attacked.

Acetobromomaltose is reduced by means of zinc dust and 50% acetic acid, giving a poor yield (50%) of impure acetomaltal. The latter, when boiled with water, gives *penta-acetylmaltal hydrate*, needles, m. p. 173—174° (corr.); when acetylated, it gives a *hexa-acetate*, m. p. 155—157°. The elimination of the acetyl groups from acetomaltal, followed by oxidation using perbenzoic acid, gives a disaccharide containing mannose, perhaps 6-glucosido-mannose (details will be given later).

When a solution of rhamnal in *N*-sulphuric acid is continuously extracted with ether at 35°, a yellow liquid is removed; the aqueous solution then contains l-*rhamnodeose* (2-*deoxy*-l-*rhamnose*), a colourless liquid. This substance is very readily decomposed by the action of mineral acids. It gives the pine-shaving reaction, and reduces Fehling's solution. It is converted by keeping at 20° with methyl-alcoholic hydrogen chloride into its *methyl*cyclo*acetal*, b. p. 120—130°/0·2 mm., which undergoes fission when boiled with aqueous hydrochloric acid. When rhamnodeose is oxidised by means of aqueous bromine solution, the product is *rhamnodesonic*

acid, which is isolated as its *barium* salt, colourless needles, or as the *phenylhydrazide*, m. p. 172—172·5° (corr.). Kiliani's digitoxose is therefore not identical with *l*-rhamnodeose.

It is proposed (cf. Bergmann, Schotte, and Lechinsky, A., 1922, i, 227) that, in naming a reducing disaccharide, the name of the sugar containing the intact aldehydic group should end in "ose," whilst the second constituent should be named as a glucosidic substituent, *e.g.*, 5-galactosidomannose. If both the reducing groups are glucosidically bound, as in trehalose, a name such as glucosido-glucoside is advocated. Thus sucrose becomes glucosidofructoside, or, alternatively, fructosidoglucoside, but raffinose is called galactosido-(glucosidofructoside). The terms anhydro-sugar, anhydrobiose, etc., are only employed when the aldehyde group, or its half-acetal form, is not involved in the anhydrisation; otherwise, one speaks of monose-anhydride, disaccharide-anhydride, etc. The points of attachment of the oxygen bridge are indicated by means of bracketed numbers. Thus the substance having the annexed formula is designated 5-galactosidomannose-anhydride [1 : 4] [1 : 2].



W. S. N.

The Action of Iodine on Several Carbohydrates. J. Vintilescu and D. Faltis (*Bul. Soc. Chim. România*, 1923, **5**, 59—63).—When powdered iodine is heated (in a steam bath) in a sealed tube with solutions of sucrose, invert-sugar, dextrose, lævulose, lactose, dextrin, glycogen, or gum arabic, the iodine passes slowly into solution during the first period of heating, and is completely converted into hydriodic acid, the solution becoming colourless. On prolonged heating, decomposition of the carbohydrate occurs, with the formation of formaldehyde, formic acid, and a brown oxidation product of the sugar. The iodine is transformed more easily by sugars containing lævulose and progressively slowly by dextrose, lactose, dextrin, glycogen, and gum arabic; the period of heating necessary to cause the same amount of final decomposition follows the same order. The reaction is more rapid the greater the concentration of the sugar solution. The action of hydriodic acid on the carbohydrates is found to be similar, but the destruction of reducing sugars formed is slower than is the case when iodine is added directly. [Cf. *B.*, 1924, 190.] J. W. B.

Wood Cellulose. E. Heuser and S. S. Aiyar (*Z. angew. Chem.*, 1924, **37**, 27—28).—The hypothesis of the identity of cellulose obtained from different sources is supported by experiments with cotton cellulose and wood cellulose. Both specimens give the same yield of pure cellulose triacetate on acetylation with glacial acetic acid, acetic anhydride, and sulphuryl chloride (cf. Barnett, A., 1921, i, 164), and on further treatment with methyl alcohol and hydrogen chloride (cf. Irvine and others, T., 1920, **117**, 1489; 1922, **121**, 1585) both triacetates give the same yield of the same α-methyl-glucoside. Hydrolysis of both samples of cellulose with 72%

sulphuric acid (cf. Ost and Wilkening, A., 1910, i, 364) and recovery of the dextrose (cf. Monier-Williams, T., 1921, **119**, 803) gives the same yield of crystalline dextrose. W. T. K. B.

The Constitution of Polysaccharides. VII. Esparto Cellulose. J. C. IRVINE and E. L. HIRST (*J. Chem. Soc.*, 1924, **125**, 15—25).—The amount of furfuraldehyde produced by the action of hydrochloric acid on esparto cellulose corresponds with the presence of 18·5% of pentosan in the dry, bleached material. This pentosan can be completely extracted with boiling 12% sodium hydroxide, and was identified as xylan by hydrolysis, in 2% sulphuric acid at 90°, to xylose. The total yield of xylose, based on optical measurements, was 75%, and the nett yield of crystalline material 35—50%, m. p. 143—144°. The latter yielded on methylation the same trimethyl β-methylxyloside as has previously been obtained from xylose. The formation of furfuraldehyde during the hydrolysis of the xylan could not be prevented. The remaining 81·5% of the esparto cellulose, after complete extraction of the pentosan with alkali, gave on acetylation cellobiose octa-acetate, and on methylation a trimethyl derivative from which 2 : 3 : 6-trimethylglucose was obtained on hydrolysis, thereby establishing the identity of the alkali-extracted material with cotton cellulose. The original esparto cellulose is more resistant to acetylation than cotton cellulose; the acetate was prepared by incorporating the material with glacial acetic acid containing a little chlorine, adding acetic anhydride, and then passing in a little sulphur dioxide and stirring, when a clear solution was obtained after twenty-four hours. The yield of acetate corresponds with 97·2% of the theoretical, assuming that the pentosan forms a diacetate and the remainder a triacetate. The acetate is softer and more sensitive to high temperature than that of cotton cellulose. On treatment with 1·5% methyl-alcoholic hydrogen chloride at 130° for 120 hours, the acetate yields a mixture of α- and β-methylglucoside and α- and β-methylxyloside, from which pure α-methylglucoside was isolated by crystallisation from alcohol. It is concluded that esparto cellulose is a mixture of 81·5% of hexose cellulose and 18·5% of pentosan, probably in the form of a solid solution. F. G. W.

Starch Iodide. A. LOTTERMOSER (*Oesterr. Chem. Ztg.*, 1924, **27**, 13; cf. A., 1922, i, 10).—Experiments are mentioned on the adsorption of tri-iodion, iodion, and iodine by starch. The curves obtained are typical adsorption isotherms. In the reaction between starch and iodine in the presence of potassium iodide, there is probably an initial adsorption followed by a further slow combination. G. W. R.

Lignosulphonic Acid and the Lactone of Waste Sulphite Liquors. S. V. HINTIKKA (*Cellulosechemie*, 1923, **4**, 93—94).—Salts of α-lignosulphonic acid with primary amines were prepared by separating the sodium lignosulphonate by salting out from waste sulphite liquors and precipitating the aqueous solution of

the product with α-naphthylamine sulphate, β-naphthylamine hydrochloride, and *o*-toluidine salt. Klason (A., 1922, i, 324) has considered the α-naphthylamine compound to be a normal ammonium salt of the sulphonic acid, and the β-naphthylamine compound a cyclic internal salt coupling the sulphonic acid and the aldehyde groups. The behaviour of these compounds towards 5% sodium hydroxide at 50° has been studied, the liberated amine being removed by extraction with ether and the lignosulphonic acid reprecipitated by acidification. No difference in the behaviour of these amine salts could be detected; the regenerated lignosulphonic acids were similar in appearance and contained only small residues of nitrogen. The crystalline substance isolated by Holmberg (A., 1921, i, 849) from waste sulphite liquors and described as a lactone has been further investigated. It occurs in the liquors from the digestion of spruce wood, but could not be detected in those from pine wood or from spruce bark. In the digestion of spruce wood, this lactone can be isolated in substantial quantity from the liquor in the early stages of digestion, but the quantity decreases towards the end of the process. J. F. B.

Preparation of Methylamine. M. SOMMELET (*Compt. rend.*, 1924, **178**, 217—219).—Methylamine hydrochloride, prepared by the methods of Brochet and Cambier or of Werner (cf. T., 1917, **111**, 844), is found to contain ammonium chloride and trimethyltrimethylenetriamine hydrochloride. It may be obtained pure by rendering alkaline, extracting with benzaldehyde, distilling the resulting benzylidenemethylamine (b. p. 180°), hydrolysing the latter with hydrochloric acid, washing the methylamine hydrochloride so obtained with alcohol to remove traces of the triamine salt, and finally crystallising twice from 88% alcohol. Pure methylamine hydrochloride has m. p. (in closed tube) 232—233·5° (corr.). E. E. T.

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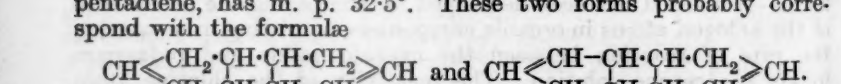
The preparation and properties of the following compounds are described: β-chloropropiophenone, from β-chloropropionyl chloride and benzene in presence of aluminium chloride, m. p. 49—50° (previous investigators have given it as 57—58°). *γ-Chlorobutyrophenone*, m. p. 19—20°. β-Phenylethyl chloride, from the corresponding alcohol and fuming hydrochloric acid at 140° for four to five hours, b. p. 68·5—69°/4 mm. *Phenylpropyl chloride*, from phenylpropyl alcohol and concentrated hydrochloric acid at 100°, b. p. 85—87°/9 mm. *δ-Phenylbutyl chloride*, b. p. 100—101°/6 mm. *ε-Phenylamyl chloride*, b. p. 111—112°/6 mm. *ζ-Phenylhexyl chloride*, b. p. 115—116°/4 mm. *Phenylheptyl chloride* was obtained only about 88% pure, from the crude alcohol and hydrochloric acid, b. p. 120—140°/3 mm. F. A. M.

Absorption of Ultra-violet Light by Organic Compounds. II. L. Marchlewski and A. Moroz (*Bull. Soc. chim.*, 1924, [iv], **35**, 37—40).—The results of studying the ultra-violet absorption spectra of alcoholic solutions of nitrobenzene, azoxybenzene, azobenzene, hydrazobenzene, and aniline are given in tables and curves. The extinction coefficients are calculated (cf. this vol., A., ii, 7). E. E. T.

The Constitution of Di*cyclo*pentadiene. H. Staudinger and A. Rheiner (*Helv. Chim. Acta*, 1924, **7**, 23—31).—Commercial di*cyclo*pentadiene can be separated by fractional distillation at a low pressure into two isomerides; the higher-boiling fraction, the β-form, has m. p. 19·5°, whilst the α-form, the known di*cyclo*pentadiene, has m. p. 32·5°. These two forms probably correspond with the formulæ



Each of these isomerides should exist in two stereoisomeric forms. The two isomerides which were isolated cannot be stereoisomerides, since by partial reduction they both give the same *dihydrodi*cyclo*pentadiene*, white crystals, m. p. 57°. This compound can be distilled at atmospheric pressure (b. p. 183·5—184·5°) and is therefore more stable than di*cyclo*pentadiene, which, under these conditions, is completely depolymerised. Dihydrodi*cyclo*pentadiene is decomposed into *cyclo*pentadiene and *cyclo*pentene when its vapour is passed over a red-hot platinum spiral. Further reduction of dihydrodi*cyclo*pentadiene gives the known tetrahydrodi*cyclo*pentadiene, which is still more stable, and is with difficulty decomposed to *cyclo*pentene. The disruption of the *cyclo*butane ring in di*cyclo*pentadiene is attributed to the influence of the double bond in the β-position to the carbon linking. A similar cause is responsible for the ready decomposition of limonene, caoutchouc, and hexaphenylethane. *Tri*cyclo*pentadiene* is obtained when di*cyclo*pentadiene is heated in a sealed tube at 170° for some hours. It forms colourless crystals, m. p. 60°, b. p. 90—92°/0·06 mm. It is more stable to heat than di*cyclo*pentadiene or *tetra*cyclo*pentadiene*. The latter is obtained by heating di*cyclo*pentadiene for a longer

time at 180°. It has m. p. 188—190°, and when heated at 180—200° decomposes smoothly into *cyclo*pentadiene. When reduced with hydrogen and platinum black, it gives *tetrahydrotetra*cyclo*pentadiene*, m. p. 200—202°, which can be distilled unchanged. Still further polymerisation of di*cyclo*pentadiene results in the production of *poly*cyclo*pentadiene*, an insoluble, infusible, white, crystalline powder, decomposing at 285°. E. H. R.

The Constitution of the Disulphoxides. I. S. Smiles and D. T. Gibson (*J. Chem. Soc.*, 1924, **125**, 176—183).—The various formulæ given to the disulphoxides at different times are discussed, and an attempt is made to decide between the symmetrical and unsymmetrical formulæ, $R{\cdot}SO_2{\cdot}SR$ and $R{\cdot}SO{\cdot}SO{\cdot}R$. Considered as a whole, the evidence at present available favours the unsymmetrical type. The reaction of mercaptans with disulphoxides is studied, and using a mercaptan $R'{\cdot}SH$, where R′ is different from the group R in the disulphoxide it is found that high yields of the sulphinic acid, $R{\cdot}SO_2H$, are obtained with a mixed disulphide, $R'S{\cdot}SR$, but no sulphinic acid, $R'{\cdot}SO_2H$. 2 : 5-*Dichlorobenzenesulphinic acid*, $C_6H_3Cl_2{\cdot}SO_2H$, forms crystals, m. p. 122°. 2 : 5 : 2′ : 5′-*Tetrachlorodiphenyl disulphoxide*, $(C_6H_3Cl_2)_2S_2O_2$, crystallises in needles, m. p. 128°; 3 : 3′-*dicarboxydiphenyl disulphoxide*, $(C_6H_4{\cdot}CO_2H)_2S_2O_2$, has m. p. 229°; 2 : 5-*dichloro*-4′-*methyldiphenyl disulphide* forms needles, m. p. 71—72°; *phenyl*-2-*naphthyl disulphide*, m. p. 74—75°; 2 : 5-*dichloro*-3′-*nitrodiphenyl disulphide*, needles, m. p. 89—91°; 9-*anthryl*-4-*tolyl disulphide*, bright yellow needles, m. p. 98—99°; 3-*carboxyphenyl*-4-*tolyl disulphide*, crystals, m. p. 140°. F. G. P.

Preparation of Diphenyl. C. H. Lowe and C. James (*J. Amer. Chem Soc.*, 1923, **45**, 2666—2669).—When using the apparatus previously described (*J. Amer. Chem. Soc.*, 1917, **39**, 933) for the preparation of diphenyl, difficulties arise owing to local heating and sagging of the filament of the heating element, with resulting short-circuiting. A filament support is now described in which these defects are eliminated. It is claimed that by maintaining the filament at a yellowish-red heat very good yields of diphenyl may be obtained from commercially pure benzene, which need not be anhydrous. The addition of more water does not hasten the reaction. W. S. N.

Anthracenemonosulphonic Acids. Sulphonation of Hydrocarbons in a Basic or Neutral Medium. M. Battegay and P. Brandt (*Bull. Soc. chim.*, 1923, **33**, [iv], 1667—1678; cf. A., 1922, i, 1001).—In the direct sulphonation of anthracene by means of fuming sulphuric acid or chlorosulphonic acid, the separation of the two isomeric anthracenemonosulphonic acids is effected by means of the barium in preference to the sodium salts. The position of the entering sulphonic group was determined by conversion of the acids into the corresponding α- and β-chloroanthraquinones under the influence of nascent chlorine. The two acids are formed in almost equal proportions; elevation of temperature does not appear to favour a greater production of the β-isomeride,

as in the case of naphthalene (Fierz and Weissenbach, A., 1920, i, 430), although accurate observation is difficult by reason of the disulphonation of anthracene at temperatures above 100°. When, however, anthracene-α-sulphonic acid was heated in 96% sulphuric acid at temperatures ranging from 150—180° and subsequently transformed into dichloroanthraquinone, the product appeared to consist wholly of the 1 : 5- and 1 : 8-isomerides, thus indicating that no shifting of the sulphonic group from the α- to the β-position had occurred. Sulphonation in presence of mercury, mercurous sulphate, or mercurous oxide resulted in a slight increase in yield without any appreciable effect on the relative proportions of the isomerides. Attempts at sulphonation in a neutral or basic medium (cf. Battegay and Brandt, A., 1922, i, 1001) were made, pyridine being used as the medium in place of the acetic acid employed in the work described above. Experiments were carried out over a temperature range of 95—115° and with varying proportions of the solvent. The best yields were obtained when a portion of the pyridine was replaced by a neutral solvent of higher b. p. In the presence of petroleum at 165—175°, almost the whole of the resulting anthracenesulphonic acid is the α-isomeride, and the addition of mercury compounds has no appreciable influence on the yield or the course of the reaction. When nitrobenzene is used, the yield is considerably smaller. A brief note on the application of Wagner's theory (A., 1886, 708) to the mechanism of the reaction is appended.

Anthracene-α-sulphonic chloride, m. p. 90°, was prepared, but probably in an impure condition; on being heated with alcoholic ammonia, it yields the corresponding *sulphonamide*, brown crystals, m. p. 205° (cf. Heffter, A., 1895, i, 671). H. J. E.

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. IV. Action of the Alkali Metals on Triphenylmethyl and its Compounds. C. A. Kraus and T. Kawamura (*J. Amer. Chem. Soc.*, 1923, **45**, 2756—2763).—The strongly electropositive metals react with triphenylmethyl chloride in liquid ammonia forming the compound of the metal with the triphenylmethyl group, *e.g.*, $CPh_3{\cdot}Na$. The *sodium* compound has been obtained in red needles. With ammonium chloride in liquid ammonia the sodium derivative gives an immediate pink precipitate which turns white on standing owing to production of triphenylmethane, $CPh_3{\cdot}Na \longrightarrow CPh_3{\cdot}NH_4 \longrightarrow CPh_3H + NH_3$. The sodium compound is unstable, but the *potassium* derivative is stable even at 100°. Triphenylmethyl is obtained by the action of triphenylmethyl chloride on sodium triphenylmethyl in the presence of toluene; this reaction does not take place if the sodium compound is replaced by the potassium derivative. Bromobenzene converts sodium triphenylmethyl into tetraphenylmethane. The mechanism of the reduction of organic halides by means of the alkali metals in liquid ammonia solution is discussed.

F. G. P.

The Preparation and Properties of Organic Stannichlorides. VI. The Action of Sulphuric Acid on certain Stannichlorides. The Formation of Stannisulphates. J. G. F. DRUCE (*Chem. News*, 1924, **128**, 33—34; cf. A., 1922, i, 1206).—Stannisulphates of some organic bases can be obtained by the action of concentrated sulphuric acid on the corresponding stannichloride. The stannisulphate crystallises from the sulphuric acid after the addition of ether. *Aniline stannisulphate*, $(PhNH_2)_2,H_2Sn(SO_4)_3$, forms grey, deliquescent crystals. m-*Phenylenediamine stannisulphate*, $C_6H_4(NH_2)_2,H_2Sn(SO_4)_3$, does not melt below 300°. *Quinoline stannisulphate*, $(C_9H_7N)_2,H_2Sn(SO_4)_3$, forms colourless, deliquescent needles, m. p. 124°. Potassium and calcium stannisulphates can be prepared in the same way from the stannichlorides. E. H. R.

The Mechanism of the Hofmann Rearrangement of Methylaniline Hydrochloride. J. W. HOWARD and C. G. DERICK (*J. Amer. Chem. Soc.*, 1924, **46**, 166—177).—The investigation was undertaken to confirm Hofmann's original views as to the nature of the change (*Ber.*, 1871, **4**, 742). It was found that in the rearrangement methyl chloride dissociates from the methylaniline hydrochloride and combines with a second molecule, forming phenyltrimethylammonium chloride; this compound then undergoes rearrangement. No rearrangement takes place at 220—250° unless the heating is continued for ninety-six hours. At 300°, however, rearrangement takes place, and is somewhat affected by time, but temperature is the chief factor. Neither methylaniline nor dimethylaniline rearranges. A quantitative separation and determination of the three classes of amine by means of benzenesulphonyl chloride has been worked out. F. A. M.

***p*-Bromophenyltrimethylammonium Perhalides.** T. H. READE (*J. Chem. Soc.*, 1924, **125**, 148—157; cf. T., 1923, **123**, 141).—The degradation of perhalides by acetone has yielded analogous quaternary ammonium salts in the case of this series, the corresponding *p*-iodo series, and the simple phenyltrimethylammonium series itself, the part removed by acetone being either iodine chloride or bromide or chlorine. The points of difference between the *p*-bromo-series and the unsubstituted series are that *p*-bromophenyltrimethylammonium bromide di-iodide yielded the *p*-bromophenyltrimethylammonium bromide on treatment with acetone, whereas its analogue in the unsubstituted phenyl series was not attacked, and that well-defined double perhalides have been obtained in several reactions. Chlorine replaces *N*-halogen in iodides and periodides, replaces *N*-bromine only when iodine is also present, and replaces added halogens in perbromides. Both bromine and iodine replace *N*-chlorine to an appreciable extent, and iodine replaces *N*-bromine in one instance. p-*Bromophenyltrimethylammonium methyl sulphate*, $C_6H_4Br{\cdot}NMe_3{\cdot}SO_4Me$, white crystals, m. p. 208°, when treated with bromine in hydrobromic

acid solution, gives the *perbromide*, $C_6H_4Br\cdot NMe_3Br_3$, orange-red leaflets, m. p. 175°. When warmed with acetone this perbromide yields the *bromide*, $C_6H_4Br\cdot NMe_3Br$, m. p. 210°. Iodine in acetic acid gave $C_6H_4Br\cdot NMe_3Br,IBr$; chlorine similarly yielded

$$C_6H_4Br\cdot NMe_3Br\cdot Cl_2,$$

lemon-yellow plates, m. p. 158°. The bromo-dichloride, the perbromide, and the bromodi-iodide are obtained by the action of halogens on the simple bromide of m. p. 210°. Chlorine with the *p*-bromophenyltrimethylammonium iodide gives the *chloride iodotrichloride*, $C_6H_4Br\cdot NMe_3Cl,ICl_3$, m. p. 187°, bromine gives the *bromoiodobromide*, m. p. 185°, iodine the *tri-iodide*, m. p. 172°. The *chloride iodochloride*, $C_6H_4Br\cdot NMe_3Cl,ICl$, m. p. 177°, is obtained by the action of chlorine on the simple iodide, and on treatment with bromine gives a yellow double perhalide,

$$C_6H_4Br\cdot NMe_3Cl,ICl + C_6H_4Br\cdot NMe_3Br,ICl.$$

Acetone converts the chloride iodochloride into the simple *chloride*, m. p. 199°; this with iodine gives the double compound, $C_6H_4Br\cdot NMe_3I_3 + C_6H_4Br\cdot NMe_3I_5$. The *bromide iodobromide*, $C_6H_4Br\cdot NMe_3Br,IBr$, obtained by the action of bromine on the iodide, crystallises in orange plates, m. p. 189° (decomp.). With chlorine, it yields $C_6H_4Br\cdot NMe_3Cl,ICl_3$; bromine has no action, iodine gives a red double perhalide, $C_6H_4Br\cdot NMe_3Br,IBr + C_6H_4Br\cdot NMe_3BrI_2$. The *bromide di-iodide*, $C_6H_4Br\cdot NMe_3BrI_2$, obtained by the action of iodine on the bromide, has m. p. 172° (decomp.). With chlorine, it yields yellow needles of

$$C_6H_4Br\cdot NMe_3Cl,ICl_3,$$

m. p. 186°, with bromine, the *bromide iodobromide*, m. p. 189°, and with iodine the tri-iodide. The *bromide iodochloride*, $C_6H_4Br\cdot NMe_3Br,ICl$, is obtained by the action of iodine monochloride on the bromide, in the form of yellow crystals, m. p. 178—179°. With chlorine, it yields $C_6H_4Br\cdot NMe_3Cl,ICl_3$, m. p. 186°; with bromine a mixture of the bromide iodobromide and bromide iodochloride, and with iodine a mixture of bromide di-iodide and bromide iodochloride. The *bromide dichloride*, $C_6H_4Br\cdot NMe_3Br,Cl_2$, results by the action of chlorine on the bromide. It forms greenish-yellow crystals, m. p. 158°. Neither chlorine nor bromine has any action on it; with iodine, it yields the *bromide iodochloride*, m. p. 178°. [F. G. P.

p-Iodophenyltrimethylammonium Perhalides. T. H. Reade and S. A. Sim (*J. Chem. Soc.*, 1924, **125**, 157—160).—Chlorine converts *p*-iodophenyltrimethylammonium iodide into the chloride iodotrichloride, $C_6H_4INMe_3Cl\cdot ICl_3$, and this can be degraded by ethyl malonate, yielding the dichloro-iodide, $C_6H_4I\cdot NMe_3Cl\cdot ICl$. With hot glacial acetic acid, the dichloro-iodide yields a double perhalide, $C_6H_4I\cdot NMe_3Cl_2I + C_6H_4I\cdot NMe_3ClI_2$. *p-Iodophenyltrimethylammonium chloride iodotrichloride*,

$$C_6H_4I\cdot NMe_3Cl\cdot ICl_3,$$

crystallises in yellow needles, m. p. 187°; on treatment with ethyl malonate under reduced pressure it gives the *chloride–iodochloride*, yellow crystals, m. p. 184°. The *tri-iodide* crystallises in brown

leaflets, m. p. 189°. A method for determining the ionisable halogen in the perhalides is given. F. G. P.

Synthesis of Indanylamine and of its *N*-Substituted Derivatives. C. COURTOT and A. DONDELINGER (*Compt. rend.*, 1924, **178**, 493—495; cf. A., 1923, i, 1090).—1-Chloroindane is converted by dry liquid ammonia in a closed vessel, at the ordinary temperature, into 1-indanylamine, b. p. 96—97°/8 mm., and a little di-indanylamine, m. p. 84—85°. Methyl-, dimethyl-, ethyl- and diethyl-amines similarly convert chloroindane into *methylindanylamine*, b. p. 106—107°/15 mm., *dimethylindanylamine*, b. p.1 00°/10 mm., *ethylindanylamine*, b. p. 106—107°/7 mm., and *diethylindanylamine*, b. p. 112—113°/8 mm., respectively, all four amines being colourless liquids.

Indene, on hydrogenation in presence of platinum black, affords indane (in 97% yield), which does not react with magnesium ethyl bromide at 135° (cf. Grignard and Courtot, A., 1911, i, 193). The reactivity of the methylene group in indene is therefore due to the presence of unsaturation in the 5-membered ring. E. E. T.

Preparation of 3 : 3′-Diaminodiphenylsulphone by Electrolytic Reduction of 3 : 3′-Dinitrodiphenylsulphone. J. LACROIX (*Compt. rend.*, 1924, **178**, 483—486).—The electrolytic reduction of 3 : 3′-dinitrodiphenylsulphone to the diamino-derivative is best effected (yield, 94·5%) by the use of an alcoholic solution of the dinitro-compound acidified wth hydrochloric acid as the cathode liquid, with a cathode consisting of nickel foil covered with spongy tin. The anode is of lead immersed in 10% sulphuric acid. The cathode liquid is maintained at a temperature of 68—72° and well agitated. A. B. H.

Chloronitrobenzenes and Thiocarbamides. J. TAYLOR and A. E. DIXON (*J. Chem. Soc.*, 1924, **125**, 243—250).—Neither *o*- nor *p*-chloronitrobenzene nor 2 : 5-dichloronitrobenzene combines with thiocarbamide. 1-Chloro-2 : 4-dinitrobenzene unites with thiocarbamide and with phenylthiocarbamide to form additive salts, from which alkali hydroxides eliminate hydrogen chloride, the dinitrophenyl residue breaking off as dinitrophenyl mercaptan. With thiocarbanilide, chlorodinitrobenzene gives mainly phenylthiocarbimide and dinitrodiphenylamine, $(NO_2)_2C_6H_3$·NHPh. Picryl chloride unites with thiocarbamide to form an *additive* compound, from which a *picrate* and a *salicylate* were obtained. Phenylthiocarbamide gave little additive salt, thiocarbanilide none. The picryl compounds are unstable, decomposing readily into dipicryl sulphide and a dark-coloured powder. In no case was an *N*-substituted thiocarbamide obtained, the behaviour of dinitrochlorobenzene and picryl chloride thus more resembling that of an alkyl halide than of an acid chloride. The *picrates* of the compounds obtained from 1-chloro-2 : 4-dinitrobenzene with thiocarbamide and phenylthiocarbamide are yellow compounds, m. p. 192—193° and 160—161°, respectively. The *picrate* derived from picryl chloride and thiocarbamide has m. p. 149—150°, the *salicylate*, m. p. 76°. F. G. P.

The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. I. The Reaction between Phenylmethylcarbamyl Chloride and Ethyl Alcohol at Different Temperatures. T. W. PRICE (*J. Chem. Soc.*, 1924, **125**, 115—129).—The reaction between phenylmethylcarbamyl chloride (m. p. 87·5°) and alcohol is very slow at temperatures below the boiling point of alcohol, and was consequently studied in sealed tubes at 100°, 90°, 80°, and 70°. Under these conditions, the carbamyl chloride first reacts with the alcohol to form phenylmethylurethane together with hydrogen chloride, which then reacts further with alcohol to form ethyl chloride and water. The first reaction was studied separately by adding dimethylaniline to the reaction mixture to combine with the hydrogen chloride and prevent the formation of ethyl chloride. The velocity of the reaction between the alcohol and the carbamyl chloride was found to vary with the amount of dimethylaniline added, being slower in presence of more base. Three series of experiments were therefore made at 100° with different amounts of dimethylaniline, and the velocity constant of the reaction in absence of dimethylaniline was found by extrapolation to be k_1=0·0426 at 100°. As this value was in good agreement with the value obtained by calculation from the study of the combined reaction, measurements in presence of varying quantities of dimethylaniline were omitted at the other temperatures. The position of the reaction under these conditions was determined by titration of the dimethylaniline hydrochloride present at any given moment, the initial concentration of the carbamyl chloride in the alcohol being in all cases $N/2$. The action of hydrogen chloride ($N/2$) on ethyl alcohol was investigated separately. The velocity constant fell steadily at each temperature, the means of the first three values being k_2 = 0·0102 at 100°, 0·00443 at 90°, 0·00162 at 80°, and 0·000521 at 70°.

The whole reaction was then studied by determining the amounts of carbamyl chloride, hydrogen chloride, and ethyl chloride present at any instant. The hydrogen chloride was determined by direct titration, and the carbamyl chloride by hydrolysis with excess of potassium hydroxide after removal of the ethyl chloride, followed by titration with silver nitrate. The velocity constants of the first reaction, calculated from the amounts of carbamyl chloride present, were k_1=0·0427 at 100°, 0·0196 at 90°, 0·00873 at 80°, and 0·00329 at 70°. Expressions deduced for the amounts of the various reactants present at any time from the values of k_1 and k_2, as well as for the maximum amount of hydrogen chloride present and the time taken for this maximum to be reached, gave satisfactory agreement with experimental results, and the variation of temperature coefficient for each reaction was shown to be in accordance with Lewis' deductions. F. G. W.

Esterification of *cyclo*Hexanol and of some of its Homologues. (MLLE.) G. CAUQUIL (*Compt. rend.*, 1924, **178**, 323—326).—*cyclo*Hexanol, 2-methyl*cyclo*hexanol, or 3 : 4-dimethyl*cyclo*hexanol was heated, at 95°, with an equivalent weight of acetic

acid until equilibrium was attained, when it was found that 55·6%, 49·8%, and 47·5% of the three alcohols, respectively, had undergone esterification. E. E. T.

The Catalytic Hydrogenation of Organic Fluoro-derivatives. III. The Hydrogenation of ω-Trifluoro-*m*-cresol. F. SWARTS (*Bull. Soc. chim. Belg.*, 1923, **32**, 367—376; cf. A., 1921, i, 656).—The hydrogenation of ω-trifluoro-*m*-cresol in the presence of platinum black proceeds in two directions, one resulting in the formation of ω-trifluoromethyl*cyclo*hexanol, the other in the production of ω-trifluoromethyl*cyclo*hexane and water, the group CF_3– being unaffected. The relative proportions of the *cyclo*hydrocarbon and *cyclo*alcohol are not constant, increase of temperature favouring the production of the hydrocarbon. In the case of ω-trifluoro-*m*-cresol, a thermal coefficient of acceleration is observed, whilst the velocity of absorption of the hydrogen by the trifluoromethyl*cyclo*hexane varies little with the temperature. An attempt is made to deduce a formula by means of which the thermal coefficient of the reaction can be calculated.

*Trifluoromethyl*cyclo*hexan*-3-*ol*, $CF_3 \cdot C_6H_{10} \cdot OH$, is a viscous liquid, b. p. 183—184°; its *benzoyl* derivative crystallises in prisms, m. p. 55°, d^{17} 1·2611. The *acetyl* derivative has b. p. 192·5—194°. *Trifluoromethyl*cyclo*hexan*-3-*one* is obtained by oxidising the corresponding *cyclo*hexane with chromic acid; it boils at 173—174°/746 mm., d^{16} 1·242. Its *semicarbazone* melts at 190°. F. G. P.

The Lead Derivative of Trinitroresorcinol. C. A. TAYLOR and W. H. RINKENBACH (*U.S. Bur. Mines, Repts. Investigations*, 1923, No. 2533).—The *lead* derivative of trinitroresorcinol is obtained in 94·4% yield, as fine, light orange-coloured crystals, *d* 3·09, by mixing boiling solutions of lead nitrate, trinitroresorcinol, and sodium carbonate, to which glacial acetic acid has been added. Its explosion temperature is 293° and rate of detonation 2097—2209 m. per second. CHEMICAL ABSTRACTS.

The Influence of Hydrogen Concentration on the Autoxidation of Quinol. A Note on the Stability of the Quinhydrone Electrode. V. K. LAMER and E. K. RIDEAL (*J. Amer. Chem. Soc.*, 1924, **46**, 223—231).—The rate at which quinol reacts with molecular oxygen has been followed by shaking borate buffers, 0·01*M* with respect to quinol, with oxygen. The rate does not become appreciable until the solution is more alkaline than p_H 7·3 or 7·8 for air. The rate of reaction is highly sensitive to further increase of p_H value, being proportional to $[H^+]^{3/2}$, where $[H^+]$ is the hydrogen-ion concentration, for the region investigated. A mechanism involving complex formation of the primary and secondary ions is suggested to explain this relationship, such as: $2H_2C_6H_4O_2 \longrightarrow 3H^+ + HC_6H_4O^- + C_6H_4O^- \longrightarrow$ complex ion; complex $+ 2O_2 \longrightarrow 2$ quinone $+ H_2O_2$. F. A. M.

Arylazides. III. Quinol Ethers from *p*-Methylated Arylazides. E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1924, **7**, 112—122).—A detailed account of experiments the results of which have already been recorded (A., 1921, i, 721). E. H. R.

Arylazides. IV. Iminoquinol Ethers from *p*-Methylated Arylazides. E. BAMBERGER, J. BRUN, and A. HARTMANN (*Helv. Chim. Acta*, 1924, 7, 123—131).—A detailed account of work already published (A., 1921, i, 721). E. H. R.

Electrochemical Oxidation of Alkyl Ethers of Phenol and of the Three Isomeric Dihydroxybenzenes. F. FICHTER and W. DIETRICH (*Helv. Chim. Acta*, 1924, 7, 131—143).—Anodic oxidation of anisole in suspension in dilute sulphuric acid, using a lead peroxide anode, results in a high yield of benzoquinone, up to 71% of theory under favourable conditions. This result is obtained using a diaphragm; in absence of a diaphragm, a mixture of quinhydrone and quinol is obtained. Quinol monomethyl ether is probably formed as an intermediate product, since this is converted practically quantitatively into benzoquinone by anodic oxidation. The methyl group is oxidised to methyl alcohol. When a platinum anode is used the yield of benzoquinone is very small; some formaldehyde is formed but the principal product is carbon dioxide. Phenetole and phenyl *iso*amyl ether give smaller yields of benzoquinone, whilst the alkyl group is in each case oxidised to the corresponding acid. Quinol dimethyl ether gives benzoquinone, the best yield being 48·6% of theory.

By the oxidation of guaiacol, using a diaphragm, at first only fumaric acid could be obtained; this, in absence of a diaphragm, was reduced to succinic acid. By stopping the oxidation at an early stage, however, an oily product was obtained from which a diphenyl derivative, *diguaiacol*, was isolated. This is probably 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxydiphenyl*; it crystallises in slender needles, m. p. 166°, and gives an orange colour with ferric chloride. Its *diacetyl* derivative crystallises in leaflets, m. p. 198°, and its *dibenzoyl* derivative in white needles, m. p. 203°. By demethylation, it gives a *tetrahydroxydiphenyl* (? 3 : 4 : 3′ : 4′), needles, m. p. 134°, giving an emerald-green coloration with ferric chloride. Its *tetra-acetyl* derivative has m. p. 161°. Further methylation of diguaiacol converts it into *diveratrole*, or *tetramethoxydiphenyl*, colourless tablets or leaflets, m. p. 130°. Anodic oxidation of veratrole gives rise to some diveratrole, but in addition, partial demethylation occurs with formation of a *hydroxytrimethoxydiphenyl*, which gives an *acetyl* derivative, pale yellow leaflets, m. p. 116°. Anodic oxidation of resorcinol monomethyl ether gives an amorphous *dihydroxydimethoxydiphenyl* which, when demethylated, gives 2 : 4 : 2′ : 4′-tetrahydroxydiphenyl (2 : 4 : 2′ : 4′-diresorcinol). E. H. R.

The Catalytic Condensation of Acetylene with Phenols. H. H. WENZKE and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1924, 46, 177—181).—Acetylene condenses with phenols and cresols in 95% alcoholic solution, in presence of sulphuric acid and mercury salts, to form uncrystallisable resins. The di- and trihydroxybenzenes react even more readily. With β-naphthol, acetylene condenses to form an acetal and some ethylidenedi-β-naphthol. Resorcinol condenses with acetylene to form ethyl-

idenediresorcinol (as-2 : 4 : 2′ : 4′-*tetrahydroxydiphenylethane*), which loses water spontaneously to form 3 : 6-*dihydroxy*-9-*methylxanthene*, soluble in water and alkalis (decomp. 230—240°). On heating with stannic chloride at 160—180°, it oxidises to form 6-*hydroxy*-9-*methylfluorone*, the solutions of which resemble that of fluorescein.

The presence of nitro- and sulphonic groups prevents the absorption of acetylene by a phenolic compound. No cases have been noted where the acetylene substitutes in a meta-position to another group. Phenetole does not react with acetylene under the above conditions. F. A. M.

The Hydrobenzoin Rearrangement. I. Hydroanisoin. M. Tiffeneau and A. Orékhoff (*Bull. Soc. chim.*, 1923, **33**, [iv], 1832—1838).—According to Russell (*Annalen*, 1869, **151**, 25), hydroanisoin, on dehydration, affords deoxyanisoin (m. p. 95°). Irvine and Moodie (T., 1907, **91**, 536) found for the latter compound the m. p. 108—109°. It is now shown that Russell's compound is *dianisylacetaldehyde*, $(OMe{\cdot}C_6H_4)_2CH{\cdot}CHO$, as would have been expected (cf. Orékhoff and Tiffeneau, A., 1921, i, 566). The aldehyde (needles, m. p. 104—105°; *semicarbazone*, m. p. 140—141°) is also obtained by treating magnesium *p*-anisyl bromide with ethyl ethoxyacetate, and the product of this interaction with formic acid. On oxidation, the aldehyde affords dianisyl ketone, and with magnesium phenyl bromide gives *α-phenyl*-ββ-di-*p*-*anisylethyl alcohol* (needles, m. p. 139—140°). Hydroanisoin (m. p. 170—171°), on heating with 50% sulphuric acid, affords the above aldehyde, *iso*hydroanisoin (m. p. 125—126°) behaving similarly.

Dianisyl ketone with magnesium methyl iodide is converted into *dianisylethylene*, $(OMe{\cdot}C_6H_4)_2C{:}CH_2$ (m. p. 142—143°), the latter, when treated with mercuric oxide in presence of water and iodine, affording an iodohydrin (not isolated) which is converted by silver nitrate into deoxyanisoin. E. E. T.

Semi-pinacolic Transformation. Necessity for the Presence of the Phenyl Group in Semi-pinacolic Transformations. (Mlle.) J. Lévy (*Bull. Soc. chim.*, 1923, **33**, [iv], 1655—1666; cf. Tiffeneau and Lévy, A., 1923, i, 788, 789).—In the aromatic series, the stability of the secondary hydroxyl group in respect of semi-pinacolic transformations appears to be conditioned by the nature of the aryl group linked to the secondary carbon atom. The author has studied the dehydration of six tri-substituted glycols and draws the conclusion that in addition to transpositions involving only phenylic groups in which the shifting of a group occurs only when the group capable of migration is arylic, others take place only in the cyclic series, but this is limited to cases in which the aryl group occupies one definite position. In these cases, the migratory group may be either cyclic or acyclic. Experimental details of the dehydration of the glycols are given (cf. A., 1921, i, 860). The following substances are described: βγ-*di*-

hydroxy-α-phenyl-γ-methylbutane, needles, m. p. 64—65°; *ethyl benzylglycollate*, b. p. 170—173°/30 mm.; *benzyl isopropyl ketone*, b. p. 234—235°; *semicarbazone*, m. p. 140—141°; *α-phenyl-γ-ethylpentane-βγ-diol*, small needles, m. p. 79—80°, yielding on dehydration by means of sulphuric acid an oil, b. p. 160—170°/50 mm., which forms a semicarbazone, m. p. 160—161°; *αδ-diphenyl-γ-benzylbutane-βγ-diol*, crystals, transformed by concentrated sulphuric acid into a substance, $C_{23}H_{20}$, m. p. 94—95°, of unknown constitution; *α-methylhexane-β-ol*, b. p. 140—142°/760 mm., prepared by the action of magnesium butyl bromide on acetone, yields on dehydration a *methyl-Δ$^{\beta}$-hexene*, b. p. 95—98°/760 mm., which on treatment with hypoiodous acid yields an *iodohydrin*; this is converted into a ketone on treatment with silver nitrate without undergoing any transposition. H. J. E.

3 : 4-Dihydroxyphenylmethylaminoethanol (Adrenaline). I. Hoshino and Daiichi Seiyaku Kabushiki Kaisha (Japan. Pat. 42351).—Adrenaline is prepared from methylaminoacetyl-3 : 4-dihydroxybenzene by reducing with hydrogen, using as a catalyst colloidal solutions of metals of the platinum group, the finely powdered metals, or nickel or carbon bearing these metals. The product is purer than that obtained by Stolz's method and the yield almost theoretical. K. K.

Cyclic Trimethylene [*cyclo*Propane] Compounds. P. Bruylants (*Bull. Soc. chim. Belg.*, 1923, **32**, 358—367).—Bromination (in direct sunlight) of *cyclo*propane-1-carboxylic chloride, until the liquid boils at 135—140°, followed by treatment of the product with methyl alcohol, gives a mixture of methyl *cyclo*propane-1-carboxylate, *methyl* 1-*bromocyclopropane*-1-*carboxylate* (a colourless, mobile liquid, b. p. 168°/702 mm., d_4^{20} 1·545, n_D^{20} 1·4784), and *methyl αγ-dibromobutyrate*. The latter (b. p. 113—114°/14 mm.) is the only product of bromination in the dark, and was identified by conversion into αγ-dibromobutyramide (m. p. 80—82°). *cyclo-Propane*-1-*carboxylic anhydride*, which, on bromination, gives only open-chain derivatives, is a colourless liquid, b. p. 232°/752 mm., d_4^{20} 1·1132, n_D^{20} 1·4628. The corresponding *ethyl* ester has b. p. 178°/758 mm., d_4^{20} 1·428, n_D^{20} 1·4678. The esters are converted by ammonia into the *amide* (needles, m. p. 108°), and by concentrated sodium hydroxide into the *acid*, m. p. 77°. Magnesium methyl bromide converts the methyl ester into the *bromohydrin* (b. p. 171—172°/762 mm.), the latter with acetic anhydride giving the *bromo-acetin* (b. p. 180—182°, d_4^{20} 1·327, n_D^{20} 1·4731), and with alkali hydroxide the *oxide*, $\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!-\!CMe_2$ (O bridging), b. p. 121—125°, d_4^{20} 0·886, n_D^{20} 1·419. Digestion of the oxide with dilute sulphuric acid, followed by addition of semicarbazide, gives a *semicarbazone* (?), m. p. 115—140° (very indefinite). Electrolysis of potassium *cyclo*propanecarboxylate yields the free acid and a little *cyclo*propane. F. G. P.

Preparation and Properties of some Organic Uranyl Salts and, in particular, of Uranyl Benzoates and Salicylates. G. COURTOIS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1761—1773).—A continuation of previous work (A., 1914, i, 799, 802). When the hydroxide, UO_3,H_2O, is dissolved in a hot aqueous solution of benzoic acid, and the solution evaporated, *uranyl benzoate*, $(Ph\cdot CO_2)_2UO_2$ (yellow crystals, stable at 100°), separates, together with benzoic acid, which may be extracted with benzene. On further evaporation, the *acid* salt, $(Ph\cdot CO_2)_2UO_2,Ph\cdot CO_2H$, separates, the latter salt also being obtained if uranyl hydroxide is dissolved in boiling benzoic acid. Uranyl benzoate is sparingly soluble in water, the solution depositing a basic salt on standing. Below 5°, the saturated aqueous solution deposits the *dihydrate*, which becomes anhydrous on keeping at the ordinary temperature, and dissolves in ether to give a solution which rapidly deposits a yellow, crystalline compound, $(Ph\cdot CO_2)_2UO_2,2Et_2O$. The latter is also formed when a concentrated aqueous solution of the benzoate is shaken with ether, and slowly loses ether of crystallisation on keeping (rapidly at 100°).

Uranyl hydroxide dissolves in a hot alcoholic solution of benzoic acid, the *compound*, $(Ph\cdot CO_2)_2UO_2,EtOH$ (pale yellow crystals, from which ether displaces the alcohol of crystallisation), separating on cooling. This salt, on crystallisation from water or from chloroform, or on heating at 100°, loses its alcohol of crystallisation.

When aqueous solutions of uranyl benzoate are concentrated by protracted (hot) evaporation, a yellow, crystalline, *basic* salt, $(PhCO_2)_2UO_2,UO_3,H_2O$, separates, and may be freed from accompanying uranyl benzoate by extracting the latter with alcohol. Prolonged heating with water converts the basic salt into uranyl hydroxide.

Aqueous solutions of uranyl benzoate are unaffected by sunlight, whilst alcoholic solutions afford a violet precipitate of uranoso–uranic oxide, the latter becoming yellow on washing with water containing dissolved air.

Uranyl salicylate, $(OH\cdot C_6H_4\cdot CO_2)_2UO_2$, separates as orange-yellow crystals, readily soluble in methyl or ethyl alcohol, from the warm solution obtained by heating uranyl hydroxide with aqueous salicylic acid. The mother-liquors, on cooling, deposit the *dihydrate* of the above salt in the form of yellow crystals, giving red solutions in methyl or ethyl alcohol and becoming anhydrous at 140—150°, with slight decomposition. Aqueous solutions of uranyl salicylate, on boiling, acquire a red colour. Neither aqueous nor alcoholic solutions of the salt are affected by sunlight, a fact that distinguishes the salt from all other uranyl salts studied. E. E. T.

Stability of Solutions of some Organic Uranyl Salts in Absence or in Presence of Light. G. COURTOIS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1773—1785).—Previous results (A., 1914, i, 799 and 802; and preceding abstract) are re-stated and slightly extended. It is shown that saturated aqueous solutions of the

following uranyl salts are unstable even in absence of light, giving crystalline basic salts (already described): Formate, acetate, benzoate, glycollate, and citrate. The other uranyl salts examined (propionate, butyrate, lactate, quinate, salicylate, oxalate, and tartrate) are stable in the dark in aqueous solution.

Sunlight, in absence of air, causes the reduction of all the above salts, with the exception of the benzoate and salicylate. The stability of the latter may be due to the "antioxygen" property of the salicylate residue. Contrary to the view of Aloy and Rodier (A., 1920, ii, 182), decomposition by sunlight does not depend on the hydroxylic character of the salt, as in the case of the tartrate, since uranyl propionate, butyrate, etc., are decomposed in aqueous solution under the influence of sunlight. In these cases, the violet hydrated uranoso-uranic oxide (converted by washing with water into the oxide, $UO_3,2H_2O$), is precipitated. Alcohol (or ether) accelerates these decompositions, but does not initiate them. In the decomposition of uranyl salts of monobasic aliphatic acids, carbon dioxide and a hydrocarbon result (the formate giving carbon monoxide and dioxide). The other salts examined give rise to carbon dioxide, except the oxalate, which also affords the monoxide. In the case of the glycollate (lactate), formic acid and formaldehyde (acetaldehyde) are first formed. E. E. T.

The Isoelectric Point of *m*-Aminobenzoic Acid and its Equilibrium with Water, Acetic Acid, and Sodium Acetate. J. BARBAUDY (*Bull. Soc. chim.*, 1924, [iv], **35**, 31—37).—The equilibria in the systems: (1) *m*-aminobenzoic acid, acetic acid, and water, and (2) *m*-aminobenzoic acid, acetic acid, sodium acetate, and water have been studied at 25°, by determinations of hydrogen ion concentration, density, and viscosity in addition to solubility. From the solubility of *m*-aminobenzoic acid in pure water, the p_H of the isoelectric point for this acid is found to be 3·886. System (1) gave concordance between calculated and found isoelectric points, whilst in system (2) concordance was less good. [Cf. Michaelis and Davidsohn, A., 1911, ii, 192.] E. E. T.

Preparation of Benzyl Diphenylalkylacetates and the Corresponding Acids by Means of Sodamide and Alkyl Iodides. (MME.) P. RAMART (*Compt. rend.*, 1924, **178**, 396—397; cf. this vol., i, 171).—Benzyl diphenylacetate was dissolved in ether and heated with powdered sodamide for several hours, an alkyl halide then being added and so on. The following new compounds (in addition to some previously known) have been prepared by this method: *Benzyl αα-diphenylpropionate*, prisms, m. p. 71—72°, b. p. 230—233°/10 mm.; *benzyl αα-diphenyl-β-methylbutyrate*, m. p. 73—74°, b. p. 225°/2 mm.; *αα-diphenyl-Δγ-pentenoic* acid, prisms, m. p. 142° (*benzyl* ester, b. p. 240—242°/10 mm.; *amide*, m. p. 90—92°). E. E. T.

The Methods of Preparation of 6-Chloro-3-hydroxybenzoic Acid. V. I. MINAEV and K. M. RIPPER (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 673—679).—A further account of work already published (A., 1922, i, 162). G. A. R. K.

β-Phenoxypropionic Acid and some of its Derivatives. Chromanone. S. G. Powell (*J. Amer. Chem. Soc.*, 1923, **45**, 2708—2711).—In preparing γ-phenoxypropyl alcohol,

$$Ph{\cdot}O{\cdot}[CH_2]_2{\cdot}CH_2OH,$$

(Rindfusz, A., 1919, i, 342), an aqueous solution of sodium phenoxide, in which trimethylenechlorohydrin is completely soluble, may be used in place of an absolute-alcoholic solution; in fact, a slightly better yield (80%) is actually obtained by this method. β-Phenoxypropionic acid, $Ph{\cdot}O{\cdot}[CH_2]_2{\cdot}CO_2H$, may be obtained in yield varying between 32% and 45% by the gradual addition of potassium permanganate solution to a suspension of β-phenoxypropyl alcohol in a solution of magnesium sulphate. Its *ethyl* ester, a colourless oil, has b. p. 170°/40 mm. The acid *chloride*, a liquid of irritating odour, is obtained when the acid is gently warmed for a few seconds with only a slight excess of thionyl chloride; it reacts with aqueous ammonia, giving the *amide*, glistening needles, m. p. 119°. The action of phosphoric oxide in boiling benzene solution on the acid gives *chromanone*, $C_6H_4<\begin{matrix}O-CH_2\\ CO{\cdot}CH_2\end{matrix}$, a colourless, highly refracting liquid, b. p. 160°/50 mm., with a pleasant, lemon-like odour; it solidifies on keeping to a mass of crystals, m. p. 38·5°. Chromanone is also formed, together with a fraction of b. p. 237°/50 mm. (which is free from halogen), by the prolonged action of an excess of thionyl chloride on β-phenoxypropionic acid. Chromanone forms an *oxime*, glistening needles, m. p. 140°, and a *benzylidene* derivative, long, yellow needles, m. p. 112°. W. S. N.

The Isomeric Esters of *p*-Methoxybenzoylacrylic Acid. G. P. Rice (*J. Amer. Chem. Soc.*, 1924, **46**, 214—223; cf. A., 1923, i, 218).—In continuation of previous work on the isomeric esters of benzoylacrylic acid, the isomeric methyl and ethyl esters of *p*-methoxybenzoylacrylic acid have been examined. The stable yellow forms when exposed to sunlight in benzene solution are converted into colourless isomerides, the reverse change taking place on exposing solutions of the colourless solids, containing a crystal of iodine, to sunlight. *p*-Methoxybenzoylacrylic acid itself is transformed by sunlight to a polymeric acid. The yellow unsaturated esters are much more readily hydrolysed by sodium carbonate than the colourless isomerides, the product being methoxybenzoylacrylic acid. With cold concentrated or boiling dilute hydrochloric acid, both isomeric esters give a mixture of unsaturated acid and α-hydroxy-*p*-methoxybenzoylacrylic acid.

The esters of the *p*-methoxy-acid do not behave in the same way as the esters of the unsubstituted acid on treatment with semicarbazide. *p*-Methoxybenzoylacrylic acid itself yields a semicarbazone; the colourless esters react with semicarbazide to form additive products and semicarbazones of these additive products.

Methyl p-*methoxybenzoylacrylate*, yellow needles, m. p. 71—72°; *colourless isomeride*, needles, m. p. 62°. *Ethyl* p-*methoxybenzoylacrylate*, large, yellow crystals, m. p. 42—43°, b. p. 210—215°/11 mm.; *colourless isomeride*, m. p. 46—47°. *Methyl* αβ-*dibromo-*

p-*methoxybenzoylpropionate* from the yellow ester, m. p. 115°. *Ethyl* αβ-*dibromo*-p-*methoxybenzoylpropionate* from the yellow ester, 1st isomeride, m. p. 51°; 2nd isomeride, m. p. 66°.

Bromination of *p*-methoxybenzoylacrylic acid yielded two isomeric forms of αβ-*dibromo*-p-*methoxybenzoylpropionic acid*, m. p. 140° and 164°, respectively. The *polymeric acid*, $C_{20}H_{20}O_8$, from *p*-methoxybenzoylacrylic acid, has m. p. 180°.

α-*Hydroxy*-p-*methoxybenzoylacrylic acid* (from hydrolysis of unsaturated acid) has m. p. 122°.

The yellow methyl *p*-methoxybenzoylacrylate reacts with 1 mol. of semicarbazide and yields two isomeric *semicarbazones*, yellow needles, m. p. 165°, and colourless plates, m. p. 178°. The same yellow methyl ester on treatment with two molecular proportions of semicarbazide yields the *semicarbazone* of *methyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 178° (decomp.). *Methyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 161—162°, is obtained as a by-product in preparation of the semicarbazone, m. p. 178°, and also by treating the semicarbazone of methyl α-semicarbazido-*p*-methoxybenzoylpropionate with concentrated hydrochloric acid.

Treatment of the solid, m. p. 161°, with nitrous acid gave *methyl nitroso*-α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 132° (decomp.).

In a similar manner, the yellow ethyl ester of *p*-methoxybenzoylacrylic acid yields two isomeric *semicarbazones*, colourless crystals, m. p. 165°, and yellow crystals, m. p. 124°.

The *semicarbazone* of *ethyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 182° (decomp.), and *ethyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 173°, and the *nitroso*-compound, m. p. 124—125° (decomp.), are described.

Methoxybenzoylacrylic acid itself yields a *semicarbazone*, pale yellow solid, m. p. 216° (decomp.). F. A. M.

Constitution of Phthalonic Acid. CORNILLOT (*Compt. rend.*, 1924, **178**, 490—492).—Phthalonic anhydride is rapidly converted by acetic acid at 100° into the acetyl-ψ-phthalonic acid described by Kuroda and Perkin (T., 1923, **123**, 2094), who concluded that phthalonic acid has the phthalide structure. With this conclusion the author disagrees, since the anhydride possesses the normal structure. Acetyl chloride or acetic anhydride converts phthalonic acid into a mixture of phthalonic anhydride and acetyl-ψ-phthalonic acid, the proportions of the two products varying with the conditions of experiment. In boiling ethyl acetate solution (with acetic anhydride) or in suspension in acetyl chloride, almost pure phthalonic anhydride results, whilst the latter, on boiling for an hour with acetic anhydride, is entirely converted into the acetyl-ψ-acid. In any case (as in the work of Kuroda and Perkin), the secondary reaction is responsible for the production of the acetyl-ψ-acid. [See also Tcherniac, T., 1916, **109**, 1236.] E. E. T.

Condensations of Aldehydes with Resorcinol and some other Aromatic Hydroxy Compounds. R. N. SEN and N. N. SINHA (*J. Amer. Chem. Soc.*, 1923, **45**, 2984—2996).—The benzein

type of compound has been prepared by condensing aldehydes with resorcinol and similar substances in the presence of concentrated sulphuric acid at 100—130°. The intensity of the fluorescence of alkali solutions of these compounds varies with the number and the position of hydroxyl and carboxyl groups, the influence of hydroxyl groups being greater when they occur in the benzene nuclei associated with the pyrone ring than when they occur in the phenyl residue, whereas the opposite is the case with the carboxyl group. *Resorcinol-1′-hydroxybenzein*, $C_{19}H_{12}O_4$, has m. p. above 260°. Its *tetrabromo*-derivative forms red crystals. *Resorcinol-2′-methoxy-3′-hydroxybenzein*, $C_{20}H_{14}O_5$, is obtained from vanillin and resorcinol as a greyish-black powder, m. p. above 295°. *Gallic acid benzein*, $C_{21}H_{12}O_9$, from gallic acid and benzaldehyde, is a green, microcrystalline powder. *Resorcinolethein*, $C_{14}H_{10}O_3$, from resorcinol and paraldehyde, is a black, microcrystalline powder, m. p. above 290°. *Resorcinolphenetoleazobenzeinsulphonic acid*, $C_{27}H_{20}O_7N_2S$, from phenetoleazobenzaldehydesulphonic acid and resorcinol, does not fluoresce. *Resorcinol-p-hydroxybenzein-m-carboxylic acid*, $C_{20}H_{12}O_6$, is a yellow powder, m. p. above 295°. *β-Resorcylic acid benzein*, $C_{21}H_{12}O_7$, from β-resorcylic acid and benzaldehyde, is a yellow powder. *Resorcinol-3′-methoxybenzein*, $C_{20}H_{14}O_4$, from anisaldehyde and resorcinol, gives a red *tetrabromo*-derivative, decomposing at 200°. F. G. P.

Reduction Products of some Acids Derived from Camphor. L. Palfray (*Ann. Chim.*, 1923, **20**, [ix], 297—385).—A republication of work previously described (A., 1921, i, 418; 1922, i, 548; also Haller and Palfray, A., 1923, i, 577) with additional matter. Reduction of the dimethyl ester of carboxycamphoracetic acid by means of sodium and absolute alcohol resulted in the formation of a mixture of borneol, *camphoracetic glycol*, $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CH_2OH\\CH\cdot OH\end{matrix}$, an oil, b. p. 195—198°/14 mm., α_D^{15} +19° 57′, yielding a *phenylurethane*, colourless spangles, and the *monomethyl* ester,

$$C_8H_{14}<\begin{matrix}C(CO_2Me)\cdot CH_2\cdot CO_2H\\CH\cdot OH\end{matrix},$$

α_D^{20} +49° 22′. Similar reduction of the diethyl ester also yields borneol, the same glycol, and a substance of the formula $C_{15}H_{23}O_3$, probably a lactone, crystals, m. p. 50—51°, α_D^{14} +62° 22′. A discussion on the molecular refraction of the substances dealt with is appended. The following additional data are given. Ethyl hydrogen camphorate has m. p. 56—56·5°; the diethyl ester of carboxycamphoracetic acid has b. p. 202—204°/18 mm., $d_4^{24\cdot9}$ 1·09635, n_α^{24} 1·47354, n_D^{24} 1·47595, n_β^{24} 1·48708; the dimethyl ester $d_4^{25\cdot1}$ 1·14245, $n_\alpha^{25\cdot1}$ 1·48086, $n_D^{25\cdot1}$ 1·48347, $n_\beta^{25\cdot1}$ 1·49440. To obtain any considerable yield of reduction products from cyanocamphoric and homocamphoric esters, the reaction should be carried out at a temperature approaching 150°. This is also the case with the esters of carboxycamphoracetic acid, but only the ketonic group and the α-carbalkoxy-group are completely hydrogenated, the final product being the glycol. H. J. E.

Derivatives of Camphoronic Acid. W. F. Goebel and W. A. Noyes (*J. Amer. Chem. Soc.*, 1923, **45**, 3064—3070).—The investigation was undertaken in order to establish the structure of the various derivatives of camphoronic acid. The attempts to prepare either a dibasic amide or an anhydro-amide which would react with sodium hypobromite failed. Isomeric imide-amides were, however, obtained from the corresponding imides and have been found to react with sodium hypobromite. β-Anhydrocamphoronyl chloride reacts with ammonia to give transparent crystals of an *imide*, $C_9H_{13}O_4N$, m. p. 234·5—235°, $[\alpha]_D^{20}$ −5·40°. A *bromo-imide*, m. p. 220°, is similarly obtained from α-anhydrobromocamphoronyl chloride. *α-Camphoronamide-imide* is obtained by the action of phosphorus pentachloride and then anhydrous ammonia on α-camphoronimide. It forms transparent crystals, m. p. 235—236°, $[\alpha]_{5416}^{28}$ +11·87°. The *acid chloride* of β-camphoronimide is obtained from the imide and phosphorus pentachloride. It is a crystalline solid, m. p. 175·5—176·5° $[\alpha]_{5416}^{26}$ −18·32°. *β-Camphoronimide-amide* obtained by the action of ammonia on the β-imide chloride, is a crystalline solid, m. p. 205°, $[\alpha]_{5416}^{28}$ −13·73°. It reacts readily with sodium hypobromite. Potassium hydroxide fails to open the ring of either α- or β-camphoronimide, partial hydrolysis to the parent acid being the only reaction involved. F. G. P.

Oxidations with Ozone. I. The Preparation of Vanillin. E. Briner, R. Patry, and E. de Luserna (*Helv. Chim. Acta*, 1924, **7**, 62—74).—The possibility of utilising ozone for technical oxidations is discussed, and experiments on the oxidation of *iso*eugenol to vanillin are recorded. The oxidations were carried out by conducting a current of ozonised air at varying concentrations of ozone (5% to 19%) into a solution of *iso*eugenol in carbon tetrachloride, at temperatures from −15° to +50°. The highest oxidation efficiency obtained, in terms of ozone consumed, was 20%, at the lowest temperature. At higher temperatures, the efficiency falls off rapidly and the quantity of resinous by-product formed increases. [Cf. *B.*, Apr.] E. H. R.

Phthalaldehyde. II. L. Seekles (*Rec. trav. chim.*, 1924, **43**, 93—102; cf. A., 1923, i, 931).—Attempts were made unsuccessfully to utilise the blue colour obtained by the reaction between phthalaldehyde, ammonia, and acetic acid for the determination of small quantities of ammonia. The reaction product appears to contain at least three different coloured substances, and the tint produced varies with the proportions of the reactants.

The dioxime of phthalaldehyde has not hitherto been prepared. It is now obtained in small yield by the action of hydroxylamine on phthalaldehyde in cold alcohol. *Phthalaldioxime* forms light yellow crystals containing $2H_2O$, m. p. 105° (indistinct), decomposing at 150°. The *di*-p-*nitrophenylhydrazone* of phthalaldehyde forms an orange precipitate (α-form), m. p. 244—245° (decomp.). By treatment with gaseous hydrogen chloride in chloroform solution it is converted into a red *isomeride* (β-form), decomposing violently at

208°. Attempts to prepare *iso*quinoline by the interaction of methylamine and phthalaldehyde were not successful. E. H. R.

Amino- and Oximo-derivatives of Thymoquinone. R. M. Hixon (*J. Amer. Chem. Soc.*, 1923, **45**, 2333—2341).—It is pointed out that quinones may be expected to add ammonia (or an amine), (*a*) at the carbonyl group, by analogy with the formation of aldehyde-ammonia, or (*b*) at the ethylenic bond, as do certain unsaturated aliphatic acids, and that actually both reactions probably occur with the quinones. The intermediate additive compound, derived from an amine and a quinone, is structurally analogous to an ammonium salt; this undergoes rearrangement, the amine becoming attached in either of the two ways mentioned. Such an intermediate complex, if formed from a tertiary amine, would be incapable of rearrangement. Actually Jackson and Clarke (A., 1905, i, 908) have reported that dimethylaniline yields coloured additive products with quinones. This is now qualitatively confirmed, since an additive compound appears to be formed when thymoquinone is dissolved in dimethylaniline (2 mols.). This is apparently stable when air and solvents are excluded, but otherwise a purple tar is produced, which, on hydrolysis by means of 50% sulphuric acid, gives both mono- and di-hydroxythymoquinone. This indicates to some extent that tertiary amines may react with quinones just as do primary and secondary amines.

Directions are given for the purification of nitrosothymol and of nitrosocarvacrol. Their benzoates are, in effect, hydrolysed when treated in dry heptane solution with dry methylamine gas. The reaction, which cannot be an ordinary hydrolysis, is explained by assuming the formation of an intermediate compound, structurally similar to aldehyde-ammonia, which undergoes rearrangement to give the nitroso-derivative and *N*-methylbenzamide. These benzoates form unstable *additive* compounds with concentrated nitric acid, having the formulæ and m. p., respectively, $C_{17}H_{17}O_2N,3HNO_3$, 53°, and $C_{17}H_{17}O_2N,2HNO_3$, 65°. Thymoquinone dioxime may be prepared more conveniently by the action of hydroxylamine hydrochloride on nitrosocarvacrol, yield 70%, than by using nitrosothymol, yield 6—10%. It forms a *dibenzoate*, colourless needles, m. p. 199—200° (becomes discoloured at 170°). W. S. N.

The Addition of Mercuric Salts to αβ-Unsaturated Ketones. E. B. Middleton (*J. Amer. Chem. Soc.*, 1923, **45**, 2763—2769).—αβ-Unsaturated ketones such as benzylideneacetophenone (phenyl styryl ketone) react with but one molecule of mercuric acetate, whilst dibenzylideneacetone (distyryl ketone) containing two double linkages reacts with 2 mols. of mercuric acetate. The products obtained in alcoholic solution show that the groups ·OR and $HgOCOCH_3$ have been added. The reactions of the additive compounds show that the mercury compounds of phenyl styryl ketone have the structure Ph·CH(OR)·CH(HgX)·COPh, whilst the derivatives of distyryl ketone are

Ph·CH(OR)·CH(HgX)·CO·CH(HgX)CH(OR)·Ph.

Substitution in the nuclei does not affect the reaction of the

unsaturated ketones with mercuric acetate. Ketones of the *cyclo*propane series do not yield additive compounds. A comparison is made between the mercuric acetate additive compounds and the compounds obtained by Vorländer and Eichwald (A., 1923, i, 684), using the mercury halides. *α-Acetoxymercuri-β-methoxy-β-phenylpropiophenone*, $C_{18}H_{18}O_4Hg$, obtained by the action of mercuric acetate on phenyl styryl ketone in methyl alcohol, has m. p. 115°. The corresponding *ethoxy*-derivative has m. p. 134°. *α-Bromomercuri-β-methoxy-β-phenylpropiophenone*, $C_{16}H_{15}O_2BrHg$, m. p. 141°, is prepared by the action of potassium bromide on the acetoxy-compound. The *ethoxy*-compound has m. p. 138°. *α-Bromo-β-methoxy-β-phenylpropiophenone*, m. p. 76°, is obtained by adding bromine to the acetoxymercuric–methoxy-derivative of phenyl styryl ketone. The *ethoxy*-compound has m. p. 60—61° and the corresponding *iodo*-compounds 96° and 75—76°. Sodium methoxide converts α-bromo-β-methoxy-β-phenylpropiophenone into an oil, b. p. 200—205°/6 mm., addition of mercuric acetate to the oil yielding *diacetoxymercuridibenzoylmethane*, $C_{19}H_{16}O_6Hg_2$, m. p. 237°. The bromomethoxyphenylpropiophenone reacts with ethyl magnesium bromide to yield β-phenylvalerophenone, $C_{17}H_{18}O$, m. p. 63°. Distyryl ketone reacts with mercuric acetate to form the dimercurated compound containing two methoxy- and two mercuri-groups, m. p. 183°. *α-Acetoxymercuri-β-methoxy-β-phenyl-p-chloropropiophenone*, m. p. 124°, is obtained from mercuric acetate and *p*-chlorophenyl styryl ketone in methyl alcohol solution. F. G. P.

Preparation of 2 : 4 : 2′ : 4′-Tetrahydroxybenzophenone. J. B. Shoesmith and J. Haldane (*J. Chem. Soc.*, 1924, **125**, 113—115).—2 : 4-Diacetoxybenzonitrile is condensed with resorcinol by means of zinc chloride and dry hydrogen chloride, the resulting imine hydrochloride, $(AcO)_2C_6H_3{\cdot}C(:NH,HCl){\cdot}C_6H_3(OH)_2$, being readily hydrolysed to the required benzophenone in acid solution. A certain amount of resacetophenone and of β-resorcylamide may be recovered from the reaction mixture. *2 : 4-Diacetoxy-2′ : 4′-dihydroxybenzophenoneimine hydrochloride* gives crystals decomposing at 195°. F. G. P.

The Benzil Rearrangement. V. Cannizzaro's Reaction. A. Lachman (*J. Amer. Chem. Soc.*, 1923, **45**, 2356—2363).—In the Cannizzaro reaction, benzyl benzoate is formed from benzaldehyde, even in the presence of water, provided an excess of alkali is avoided and any considerable rise in temperature is prevented. It is suggested that dihydroxydibenzyl ether, $[CHPh(OH)]_2O$, is formed as an intermediate stage, and by a glycol rearrangement is converted into the benzoate. In the course of the investigation it was shown that by heating benzyl alcohol in a sealed tube at 210—215°, dibenzyl ether is obtained, and that bromine reacts with dibenzyl ether to produce benzyl bromide and benzoyl bromide. F. G. P.

The Isomerism of the Oximes. XV. The Alleged Fourth Benzildioxime. O. L. Brady and F. P. Dunn (*J. Chem. Soc.*, 1924, **125**, 291—296).—The work of Atack and Whinyates (T.,

1921, **119**, 1184) has been repeated, but the authors have been unable to confirm the results, no evidence of the existence of the fourth dioxime being obtained. The purely structural theory of the isomerism of the oximes suggested by Atack is criticised and the principal objections to it are stated, particularly the existence of two *O*-ethers. F. G. P.

Dioximes. XVI. G. Ponzio and V. Bernardi (*Gazzetta*, 1923, **53**, 813—817; cf. this vol., i, 54, 56).—The formation of the two benzildioximes from the two forms of phenylglyoxime by the action of phenyldiazonium chloride (A., 1923, i, 856) proves to be a reaction of general application constituting a new method of synthesising symmetrical and unsymmetrical, disubstituted glyoximes. Not only a glyoxime of the type NOH:CAr·CH:NOH, in which Ar is an aryl radical, but also methylglyoxime, reacts with many aryldiazonium chlorides with liberation of nitrogen and formation of the glyoximes, NOH:CR·CR$_1$:NOH. This reaction, which gives a yield of about 45%, is not so simple as is represented by the scheme,

$$NOH{:}CR{\cdot}CH{:}NOH + Ar{\cdot}N_2{\cdot}OH - H_2O \longrightarrow NOH{:}CR{\cdot}C(NOH){\cdot}N_2Ar - N_2 \longrightarrow NOH{:}CR{\cdot}CAr{:}NOH,$$

since there is entire lack of experimental evidence of the formation of an intermediate unstable compound with the N_2Ar group in direct union with a carbon atom. Participation in the reaction of the oximino-groups may, however, be excluded, since these pass with unaltered properties into the final products. Of special interest is the behaviour of methylglyoxime, which yields only the β-forms of glyoximes, NOH:CMe·CAr:NOH; the conclusion that it is a β-modification is thus confirmed. Thus, β-phenylmethylglyoxime (A., 1922, i, 17) may be obtained by the action of phenyldiazonium chloride on methylglyoxime in 10% sodium hydroxide solution cooled with ice.

β-*o*-*Tolylmethylglyoxime*, NOH:CMe·C(NOH)·C$_6$H$_4$Me, prepared from methylglyoxime and *o*-tolyldiazonium chloride, crystallises in white needles, m. p. 236° (slight decomp., and sublimation); its *nickel* salt, $(C_{10}H_{11}O_2N_2)_2Ni$, forms red prisms, m. p. 222°, and its *dibenzoyl* derivative, $C_{24}H_{20}O_4N_2$, prisms, m. p. 144°.

β-*p*-Tolylmethylglyoxime crystallises in white laminæ, m. p. 234—235°; Borsche (A., 1907, i, 326) gave m. p. above 230° (decomp.). Its *nickel* salt, $(C_{10}H_{11}O_2N_2)_2Ni$, forms blood-red prisms, m. p. 250—251° (decomp.), with previous browning, and its *dibenzoyl* compound, white needles, m. p. 148·5—149·5°.

β-*p*-Anisylmethylglyoxime, prepared from *p*-methoxyphenyldiazonium chloride and methylglyoxime, forms white prisms, m. p. 213° (slight decomp.). Boeris (A., 1894, i, 72) gave m. p. 206°, and Tschugaev (A., 1908, i, 554), m. p. 207°; cf. also Wieland (A., 1903, i, 837). Its nickel salt, $C_{20}H_{22}O_6N_4Ni$, crystallises in scarlet needles, m. p. 224° (cf. Tschugaev, *loc. cit.*), and its *dibenzoyl* derivative in needles, m. p. 148·5°.

β-*Phenyl*-p-*tolylglyoxime*, NOH:CPh·C(NOH)·C$_6$H$_4$Me, prepared by the interaction either of *p*-tolyldiazonium chloride and β-phenyl-

glyoxime, or of phenyldiazonium chloride and β-*p*-tolylglyoxime, crystallises in lustrous laminæ, m. p. 223—224° (partial sublimation). Its *nickel* salt, $(C_{15}H_{13}O_2N_2)_2Ni$, forms microscopic, brick-red needles, m. p. 295—297° (decomp.), and its *dibenzoyl* derivative, laminæ, m. p. 184° (slight decomp.).

β-*Phenyl*-p-*anisylglyoxime*, $C_{15}H_{14}O_3N_2$, prepared similarly, crystallises in white laminæ, m. p. 223° (slight decomp.). Its *nickel* salt forms a microcrystalline, blood-red powder, m. p. 264° (decomp.), and its *dibenzoyl* derivative, laminæ, m. p. 162°.

T. H. P.

Dioximes. XVIII. L. Avogadro (*Gazzetta*, 1923, **53**, 824—828).—The dehydrogenating action of nitrogen tetroxide on the α-modifications of arylglyoximes proceeds similarly to that of the same reagent on α-phenylglyoxime (A., 1923, i, 1019, 1137). Thus, α-*p*-tolylglyoxime yields a compound which must be regarded as the oxide of *p*-toluoyl cyanide oxime since (1) with acetic anhydride it yields a monoacetyl derivative, (2) it is reduced by means of zinc and acetic acid, giving *p*-toluoyl cyanide oxime, (3) when heated with xylene it undergoes isomerisation to 5-hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole, (4) it unites with a molecule of ammonia to form amino-α-*p*-tolylglyoxime, and (5) it reacts with magnesium methyl iodide to form *p*-tolylmethylglyoxime.

The *oxide* of p-*toluoyl cyanide oxime*, $NOH{:}C(C_6H_4Me)\cdot C\leqslant^{O}_{N}$, or $NOH{:}C(C_6H_4Me)\cdot C{:}N{:}O$, crystallises in silky, white needles, m. p. 108° with previous softening, and is highly stable towards acids, but is readily decomposed by bases or even by boiling water, giving *p*-toluonitrile and substances having the odour of carbylamine. Its *acetyl* derivative forms white prisms, m. p. 157—158°.

Amino-α-p-*tolylglyoxime*, $C_6H_4Me\cdot C(:NOH)\cdot C(:NOH)\cdot NH_2$, crystallises in white laminæ, m. p. 173—174°, and, when treated in aqueous alcoholic solution with nickel acetate, gives a greyish-green precipitate soluble in dilute acetic acid. When boiled with dilute acetic acid it slowly undergoes isomerisation into amino-β-*p*-tolylglyoxime, which has not been investigated further. T. H. P.

Ketens. XLVII. The Constitution of Dimeric Ketens, a Contribution to the Valency Problem of Organic Chemistry. H. Staudinger (*Helv. Chim. Acta*, 1924, **7**, 3—8).—A reply to Schroeter (A., 1920, i, 852), who criticises the author's conception of the dimeric ketens as *cyclo*butan-1 : 3-diones or 1 : 3-*cyclo*butenolones, and considers them to be molecular compounds. The conception of dimeric aldoketens as 1 : 3-*cyclo*butenolone derivatives is supported by their physical properties and absorption spectra. Schroeter considers the more stable dimeric ketens to be true *cyclo*butandiones, the less stable to be molecular compounds, but it is pointed out that *cyclo*butane derivatives differ much in their stability to heat; substitution, including the keto-group, weakens the ring, and heavily substituted compounds such as ethyl diethyl-*cyclo*butandionedicarboxylate are especially labile. The author's

view is also supported by preparation of *cyclo*butane derivatives by the combination of diphenylketen with ethylenic compounds (A., 1920, i, 556, and following abstract). E. H. R.

Ketens. XLVIII. *cyclo*Butane Derivatives from Diphenylketen and Ethylenic Compounds. H. STAUDINGER and A. RHEINER (*Helv. Chim. Acta*, 1924, **7**, 8—18).—The compound formed by diphenylketen with styrene is now found to be 1 : 1 : 4-*triphenyl*cyclo*butan*-2-*one*, $\begin{matrix}CHPh\cdot CPh_2\\ |\quad\quad |\\ CH_2\text{—}CO\end{matrix}$, instead of the 1 : 1 : 3-compound as previously stated (Staudinger and Suter, A., 1920, i, 556). It follows that the acid obtained by treating it with sodium hydroxide in alcoholic solution is αα*β-triphenyl*-n-*butyric acid* instead of the αα*γ*-compound. Evidence for the constitution of the triphenyl*cyclo*butanone was obtained through the action of methyl magnesium iodide, by means of which the tertiary alcohol, 1-*methyl*-2 : 2 : 3-*triphenyl*cyclo*butan*-1-*ol* was obtained, colourless crystals, m. p. 132°; the yield was 87% of the theoretical. When rapidly distilled at the ordinary pressure, the tertiary alcohol decomposes to the extent of 80% into *as*-diphenylacetone and styrene and 20% into acetone and triphenylethylene. These products establish its constitution. When distillation is carried out in a high vacuum, decomposition does not take place, but an *isomeride* is formed, m. p. 137°; in all probability the ring has opened with formation of a triphenyl-*n*-propyl methyl ketone. By the action of phenyl magnesium bromide on the triphenyl*cyclo*butanone there is obtained, not the expected tertiary alcohol, but *benzylidenediphenylacetone*, $CHPh_2\cdot CO\cdot CH{:}CHPh$ [*benzhydryl styryl ketone*], m. p. 112°, b. p. 250°/18 mm. The same compound was synthesised from diphenylacetone and benzaldehyde (cf. Rack, A., 1923, i, 681).

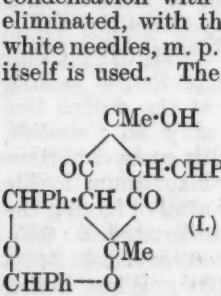
As previously described (*loc. cit.*), diphenylketen combines with *cyclo*pentadiene to form a compound, which can be reduced to a saturated compound, for which the formula $CH_2<\begin{matrix}CH_2\cdot CH\text{—}CO\\ |\quad\quad |\\ CH_2\cdot CH\text{—}CPh_2\end{matrix}$, is now proposed. When this is submitted to prolonged boiling with sodium hydroxide, hydrolysis takes place at the dotted line with formation of *diphenyl*cyclo*pentylacetic acid*, m. p. 85°; *anilide*, m. p. 139°. The compound of diphenylketen with *cyclo*pentadiene reacts with methyl magnesium iodide to give the tertiary alcohol having the annexed formula, designated 6 : 6-*diphenyl*-7-*methyl*-0 : 2 : 3-bicyclo-3 : 4(?)-*hepten*-7-*ol*, m. p. 130°. When boiled with alcoholic potassium hydroxide the heptane ring opens, probably at the dotted line, forming a *ketone*; its semicarbazone has m. p. 115°. By treatment with hydrogen and platinum black, the above heptenol is reduced to the corresponding *heptanol*, m. p. 99°. By the action of phenyl magnesium iodide on the diphenylketen–*cyclo*pentadiene compound, a *substance* was obtained, m. p. 214°, having the same empirical composition as the original compound. It may be a

$$\begin{matrix}&&&&&&^{2}&&^{1}&&^{7}\\ ^{3}CH&<&CH_2\cdot CH&\text{—}&CH&\text{—}&CMe(OH)\\ &&CH\text{—}CH&\text{—}&CPh_2&&\\ &&^{4}\quad ^{5}&&^{6}&&\end{matrix}$$

dimeride. Diphenylketen and di*cyclo*pentadiene form a *compound*, m. p. 95°. E. H. R.

Ketens. XLIX. *cyclo*Butane Derivatives from Dimethylketen and Ethylenic Compounds. H. STAUDINGER and P. J. MEYER (*Helv. Chim. Acta*, 1924, **7**, 19—22).—Dimethylketen combines less readily with ethylenic compounds than diphenylketen, but the compounds when formed are more stable than those from diphenylketen. The four-membered ring is relatively stable and the ketonic group has normal properties. Dimethylketen does not combine with styrene, but with vinyl ethyl ether it forms 3(or 4)-*ethoxy*-1 : 1-*dimethyl*cyclo*butan*-2-*one*, a colourless oil, b. p. 166—169°; the *phenylhydrazone* forms white needles, m. p. 70°, and quickly decomposes in the air. With *cyclo*pentadiene, dimethylketen forms a *compound* probably having the formula $CH\begin{matrix}CH_2\cdot CH\cdot CO\\ CH\text{—}CH\cdot CMe_2\end{matrix}$, but the position of the double bond is uncertain; it is an oil with a camphor-like odour, b. p. 175—178°; when superheated it decomposes into dimethylketen and *cyclo*pentadiene. Its *semicarbazone* has m. p. 215°. When reduced with hydrogen and platinum black it gives the saturated compound, 6 : 6-*dimethyl*-0 : 2 : 3-bicyclo*heptan*-7-*one*, also having the odour of camphor, b. p. 176—178°; it gives dimethylketen when superheated. Its *semicarbazone* has m. p. 224°. E. H. R.

Reaction Products from Aldehydes and 1 : 2-Diketones. O. DIELS [with R. W. POINDEXTER, K. ILBERG, and W. GÄDKE] (*Annalen*, 1923, **434**, 1—20).—When a mixture of benzaldehyde and diacetyl is treated at — 10° with 25% methyl-alcoholic potassium hydroxide solution, the diketone first polymerises to its dimeride, 1 : 4-dihydroxy-1 : 4-dimethyl*cyclo*hexan-3 : 6-dione (Diels, Blanchard, and v. d. Heyden, A., 1914, i, 1052); this then undergoes condensation with the aldehyde (3 mols.), 1 mol. of water being eliminated, with the formation of the same *compound* (I), slender, white needles, m. p. 198° (decomp.), which is obtained if the dimeride itself is used. The structure of this substance is evident from the following reactions. Although, probably owing to steric hindrance, the ketone groups are not reactive, the hydroxyl group next to the phenyl radical can be esterified. The *benzoate* forms thick, transparent prisms, m. p. 192°; the *acetate*, four-sided tablets or prisms, has m. p. 197—198°. But if, in preparing the acetate, the action of acetic anhydride is continued, water is eliminated, with the production of the unsaturated *acetate*, –OC·CMe:C(CHPh·OAc)·CO–, m. p. 237°. This compound reacts immediately with potassium permanganate in glacial acetic acid solution, or with bromine in cold chloroform solution; the subsequent spontaneous elimination of hydrogen bromide from the dibromide produced in the latter reaction gives two *bromo*-derivatives, $C_{31}H_{27}O_6Br$, (*a*) colourless needles, or



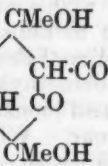
(I.)

small, elongated plates, m. p. 193°, (*b*) small, transparent prisms, m. p. 210°. The action of phenylhydrazine in methyl-alcoholic glacial acetic acid solution at 65° on the unsaturated acetate gives the corresponding unsaturated *alcohol*, m. p. 198—203°, $+x$EtOH, long prisms, which is readily converted into the compound (I) by boiling with hydrochloric, acetic, or propionic acid, and gives the saturated *methyl* ether, −OC·CMe(OMe)·CH(CHPh·OH)·CO− (felted needles, m. p. 240°, after decomposing at 218°), when boiled with methyl alcohol containing a trace of hydrochloric acid. Similarly, the action of acids on the unsaturated acetate gives the saturated acetate, which, like the analogous benzoate, is readily hydrolysed to the compound (I) by means of boiling alcoholic potassium hydroxide solution. By the action of a boiling mixture of glacial acetic acid and concentrated nitric acid on the compound (I), the secondary alcohol group is oxidised to a ketone group,

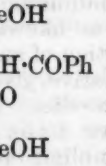
−CO·CMe(OH)·CH(COPh)·CO−,

with the formation of a *compound*, m. p. 203—204° (decomp.), which crystallises from acetonitrile with 1MeCN, in rhombic crystals, readily soluble in alkali. In 25% methyl-alcoholic potassium hydroxide solution, benzaldehyde is rapidly eliminated, with the production of the *compound* (II), thin, felted needles, m. p. 151—153° after sintering at about 146°. The latter is soluble in aqueous alkali, but soon resinifies, more rapidly on warming, with the elimination of benzaldehyde. It is converted by the action of methyl alcohol containing hydrogen chloride into its *methyl* ether, compact, snow-white crystals, m. p. 169—171° (slight decomp.); methyl hydrazinecarboxylate gives a *salt*, felted needles, m. p. 130—132° (decomp.), in the formation of which, presumably, the benzoyl group has taken part in its enolic form. The ketonic groups are not reactive. The compound (II) forms an additive *compound* with cold formic acid, but the boiling, anhydrous reagent causes the elimination of water, to give 2-*benzoyl*-1 : 4-*dihydroxy*-5-*benzylidene*-1 : 4-*dimethyl*cyclo*hexan*-3 : 6-*dione* (III), a bright sulphur-yellow compound, m. p. 238—243°, one of the ketone groups of which is reactive; the *oxime*, m. p. 221—222°, *semicarbazone*, long, colourless needles, decomp. about 235°, m. p. 245—248°, and the *carbomethoxyhydrazone*, long, colourless prisms, decomp. 220°, m. p. 240—243°, are described. The compound (III) is decomposed at 250—270° into benzoyldiacetyl and benzylidenediacetyl.

(II.)



(III.)



Compounds are also prepared by condensing diacetyl with furfurol and anisaldehyde. The first forms thick, colourless needles, m. p. 203° (decomp.) after sintering at 180°; the second forms small needles, and has m. p. 203—205° (decomp.). With concentrated sulphuric acid they give, respectively, a dark reddish-purple color-

ation, which changes to brown, and an intense carmine coloration, which persists during twenty-four hours. W. S. N.

Trihydroxymethylanthraquinones. I. G. D. GRAVES and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2439—2455).—3 : 6-Dimethoxyphthalic anhydride is prepared by the action of boiling 98% sulphuric acid on the dimethyl ether of 2 : 3-dicyanoquinol, which is obtained by the action of potassium hydroxide solution and methyl sulphate on 2 : 3-dicyanoquinol.

The action of an excess of *p*-cresol on 3 : 6-dimethoxyphthalic anhydride in the presence of aluminium chloride at 70° gives 3 : 6-*dimethoxy*-2-(2′-*hydroxy*-5′-*methylbenzoyl*)*benzoic acid*, white plates, m. p. 218° (corr.), together with 12 : 15-*dimethoxy*-2 : 7-*dimethylfluoran*, white crystals, m. p. 290° (corr.). When the benzoic acid derivative is boiled with potassium hydroxide solution and methyl sulphate, the product is 3 : 6-*dimethoxy*-2-(2′-*methoxy*-5′-*methylbenzoyl*)*benzoic acid*, white needles, or colourless, truncated prisms, m. p. 203—204° (corr.), which is identical with the product from 3 : 6-dimethoxyphthalic anhydride and *p*-cresyl methyl ether (cf. following abstract). When the substituted benzoic acid and concentrated sulphuric acid are heated at 100° with a small quantity of boric acid, the colour changes from green to bluish-red, owing to the formation of 1-*hydroxy*-5 : 8-*dimethoxy*-4-*methylanthraquinone*, red needles, m. p. 224° (corr.). The latter is demethylated by boiling with glacial acetic acid and hydrobromic acid (constant-boiling), giving 1 : 5 : 8-*trihydroxy*-4-*methylanthraquinone*. When 3 : 6-dimethoxyphthalic anhydride is heated at 75° with an excess of *o*-cresol in the presence of aluminium chloride, the products are 3 : 6-*dimethoxy*-2-(2′-*hydroxy*-3′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 194° (corr.), and *o-cresol*-3 : 6-*dimethoxyphthalein*, white needles, m. p. 258° (corr.). The latter is an indicator, changing from colourless to red at p_H 9·1. The methylation of the benzoic acid gives 3 : 6-*dimethoxy*-2-(2′-*methoxy*-3′-*methylbenzoyl*)-*benzoic acid*, white needles, m. p. 178° (corr.), which is not identical with the acid formed by condensing 3 : 6-dimethoxyphthalic anhydride with *o*-cresyl methyl ether; in the latter reaction, there is also formed the *dimethyl ether* of *o*-cresol-3 : 6-dimethoxyphthalein, white needles, m. p. 202° (corr.), which is likewise produced by the methylation of the phthalein. The action of sulphuric acid, containing boric acid, on the benzoic acid derivative, gives 1-*hydroxy*-5 : 8-*dimethoxy*-2-*methylanthraquinone*, red needles, m. p. 165° (corr.), which may be demethylated to give 1 : 5 : 8-*trihydroxy*-2-*methylanthraquinone*, red needles, which sublime at 250—260°. When *o*-cresol-3 : 6-dimethoxyphthalein and 3 : 6-dimethoxyphthalic anhydride are heated at 125° with concentrated sulphuric acid, the product is 2 : 5 : 8-*trihydroxy*-1-*methylanthraquinone*, dark red needles, m. p. 270° (corr.), which is identical with the product obtained by condensing 3 : 6-dimethoxyphthalic anhydride with *o*-cresyl methyl ether, dehydrating the benzoylbenzoic acid thus obtained, and hydrolysing the resulting anthraquinone. The interaction of 3 : 6-dimethoxyphthalic anhydride and *m*-cresol at

75° in the presence of aluminium chloride gives 3 : 6-*dimethoxy*-2-(2′-*hydroxy*-4′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 233° (corr.), and 3-*hydroxy*-6-*methoxy*-2-(2′-*hydroxy*-4′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 189° (corr.). A third substance formed in the above reaction is m-*cresol*-3 : 6-*dimethoxyphthalein*, white needles, m. p. 271° (corr.), a solution of which changes from colourless to red at p_H 9·8. The conversion of 3 : 6-dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid into 1-*hydroxy*-5 : 8-*dimethoxy*-3-*methylanthraquinone*, red needles, m. p. 172° (corr.), can only be accomplished by the use of fuming sulphuric acid at 100° in the presence of boric acid. The demethylation of this dimethoxyanthraquinone by means of glacial acetic acid and hydrobromic acid gives 1 : 5 : 8-*trihydroxy*-3-*methylanthraquinone*, red needles, m. p. 227° (corr.).

The condensation of 3 : 5-dimethoxyphthalic anhydride with *m*-cresol by heating with aluminium chloride at 70° gives 3 : 5-*dimethoxy*-2-(2′-*hydroxy*-4′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 233° (corr.), and m-*cresol*-3 : 5-*dimethoxyphthalein*, which cannot be purified. The former gives, on methylation, 3 : 5-*dimethoxy*-2-(2′-*methoxy*-4′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 219° (corr.), whereas the condensation of 3 : 5-dimethoxyphthalic anhydride with *m*-cresyl methyl ether gives 3 : 5-*dimethoxy*-2-(4′-*methoxy*-2′-*methylbenzoyl*)*benzoic acid*, m. p. 233° (corr.). The action of fuming sulphuric acid and boric acid at 100° on 3 : 5-dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid leads to sulphonation, a poor yield of the expected *anthraquinone*, yellow needles, m. p. about 185°, being obtained. This substance gives a red solution in alkali, which reacts with methyl sulphate at 100° to give a *trimethoxy* compound, yellow needles, m. p. about 175—180°, which gives a red solution in concentrated sulphuric acid, and should be the trimethyl ether of emodin, if the latter has the structure suggested (*Arch. Pharm.*, 1912, **250**, 301). The action of concentrated nitric acid in glacial acetic acid solution at 50—60° on 3 : 5-dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid gives the 5′-*nitro*-derivative, pale yellow needles, m. p. 241° (corr.), but the product of the condensation of 3 : 5-dimethoxyphthalic anhydride and *o*-nitro-*m*-cresol is 3 : 5-*dimethoxy*-2-(4′-*hydroxy*-5′-*nitro*-2′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 181° (corr.).

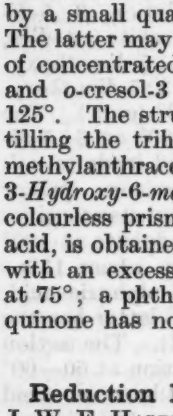
3 : 5-Dimethoxyphthalic acid is obtained by the action of cold, alkaline, potassium permanganate solution on 3 : 5-dimethoxyphthalide, which is prepared by heating its carboxylic acid. The latter is made by the action of warm sodium hydroxide solution on 3 : 5-dimethoxytrichloromethylphthalide, which is formed when a mixture of chloral hydrate and ethyl 3 : 5-dimethoxybenzoate is treated with somewhat concentrated sulphuric acid. W. S. N.

Trihydroxymethylanthraquinones. II. J. H. GARDNER and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2455—2462; cf. preceding abstract).—The action of an excess of *p*-cresyl methyl ether on 3 : 6-dimethoxyphthalic anhydride at 70° in the presence of

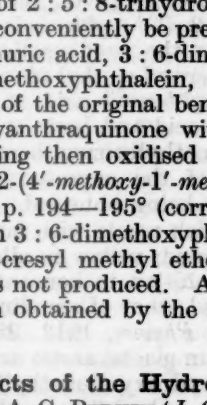
aluminium chloride gives 3 : 6-dimethoxy-2-(2′-methoxy-5′-methylbenzoyl)benzoic acid, together with the *dimethyl ether* of *p*-cresol-3 : 6-dimethoxyphthalein, colourless needles, m. p. 187·5° (corr.). When the trimethoxybenzoic acid is rapidly heated with concentrated sulphuric acid at 150°, and then cooled, the products are 1-hydroxy-5 : 8-dimethoxy-4-methylanthraquinone and 1 : 5 : 8-*trihydroxy-4-methylanthraquinone*, slender, red needles, m. p. 276—278° (corr.) (with sublimation); the latter is the sole product if the reaction mixture is kept at 145—155° for twenty minutes. When a mixture of 3 : 6-dimethoxyphthalic anhydride and an excess of *o*-cresyl methyl ether is treated at 65° with aluminium chloride, there are formed 3 : 6-*dimethoxy*-2-(4′-*methoxy*-5′-*methylbenzoyl*)*benzoic acid*, a white powder, m. p. 192° (corr.), and the *dimethyl ether* of *o*-cresol-3 : 6-dimethoxyphthalein, colourless needles, m. p. 202—203° (corr.). When the acid is rapidly heated with concentrated sulphuric acid at 150°, and immediately cooled, the chief product is 5 : 8-*dihydroxy*-2-*methoxy*-1-*methylanthraquinone*, dark red needles, m. p. 249—249·5° (corr.), which is accompanied by a small quantity of 2 : 5 : 8-trihydroxy-1-methylanthraquinone. The latter may more conveniently be prepared by heating a mixture of concentrated sulphuric acid, 3 : 6-dimethoxyphthalic anhydride, and *o*-cresol-3 : 6-dimethoxyphthalein, or its dimethyl ether, at 125°. The structure of the original benzoic acid is proved by distilling the trihydroxyanthraquinone with zinc dust, the resulting methylanthracene being then oxidised to 1-methylanthraquinone. 3-*Hydroxy*-6-*methoxy*-2-(4′-*methoxy*-1′-*methylbenzoyl*)*benzoic acid*, colourless prisms, m. p. 194—195° (corr.), and not the dimethoxy-acid, is obtained when 3 : 6-dimethoxyphthalic anhydride is treated with an excess of *m*-cresyl methyl ether and aluminium chloride at 75°; a phthalein is not produced. A pure derivative of anthraquinone has not been obtained by the dehydration of this acid.

W. S. N.

Reduction Products of the Hydroxyanthraquinones. IV. J. W. E. Haller and A. G. Perkin (*J. Chem. Soc.*, 1924, **125**, 231—239).—Reduction of 2-hydroxyanthraquinone with glucose and alkali in the presence of sodium nitrate yields 2-hydroxybenzanthrone-carboxylic acid, and two compounds which are now shown to be a 3 : 6′-dihydroxyhelianthrone, $C_{28}H_{14}O_4$ (I), and 3 : 6′-dihydroxy-*meso*naphthadianthrone, $C_{28}H_{12}O_4$ (II). Better yields of (I) are obtained by the oxidation of dihydroxydianthrone with potassium ferricyanide. (II) may be obtained by exposing the diacetyl derivative of (I) (in benzene or acetic acid solution) to sunlight for some weeks, when an almost quantitative yield of the diacetoxynaphthadianthrone



(I.)



(II.)

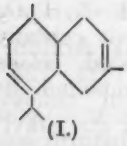
results. Oxidation of the acetyl compound of (I) with chromic acid yields *diacetoxy*-1 : 1′-*dianthraquinonyl*, $C_{28}H_{12}O_6Ac_2$, small plates, m. p. 277°. The corresponding *dihydroxy* compound crystallises in prisms or leaflets, m. p. >350°. The *dimethyl ether*, $C_{30}H_{18}O_6$, crystallises in yellow prisms, m. p. 343—344°. With iodine in pyridine solution, (I) yields 5-*iodo*-3 : 6′-*diacetoxyhelianthrone*, $C_{32}H_{17}O_6I$, yellow needles, m. p. 282°, and from this by hydrolysis the *dihydroxy* compound is obtained in the form of scarlet needles, m. p. >350°. 3 : 6′-*Dihydroxynaphthadianthrone*, $C_{28}H_{12}O_4$, is an orange-brown powder, m. p. >350°. Its *diacetyl* derivative crystallises in yellow needles. F. G. P.

Camphorylcarbamates and their Physiological Action. H. E. Fierz-David and W. Müller (*J. Chem. Soc.*, 1924, **125**, 26—27).—Camphorylcarbamates may be obtained in almost quantitative yield by the interaction of aminocamphor and alkyl chloroformates. Their pronounced poisonous action renders them unsuitable for practical application. iso*Amyl* and *allyl camphorylcarbamates* are viscous, oily liquids, b. p. 199°/11 mm., and 186°/10 mm., respectively, with $[\alpha]_D$ +34·2°, +34·3°. *Methyl camphorylcarbamate*, m. p. 110°, b. p. 169°/11 mm., $[\alpha]_D$ +39·4°. The *ethyl*, iso*propyl*, and iso*butyl* derivatives have, respectively, m. p. 88°, 73°, 83°; b. p. 178°/13 mm., 170°/10 mm., 184°/11 mm., with $[\alpha]_D$ +35·1°, 35·3°, and 33·9°. F. G. P.

Piperitone. VII. The Constitution of Piperitone. J. Read, H. G. Smith, and R. S. Hughesdon (*J. Chem. Soc.*, 1924, **125**, 129—137).—Benzyl-*dl-iso*menthone, obtained by hydrogenation of benzylidene-*dl*-piperitone, is distinct from 2-benzyl-*dl-iso*menthone obtained, from *dl*-piperitone. It is concluded from this observation that piperitone is Δ^1-*p*-menthen-3-one, and benzylidenepiperitone is 6-benzylidene-Δ^1-*p*-menthen-3-one. 6-Benzyl-*dl-iso*menthone reacts with benzaldehyde to yield 2-benzylidene-6-benzyl-*dl-iso*menthone, and it also forms a semicarbazone, whilst 2-benzyl-*dl-iso*menthone is incapable of so reacting. 2-*Benzylidene*-dl-iso*menthone hydrochloride* forms colourless needles, m. p. 108—110°. 2-*Benzyl*-dl-iso*menthol*, $C_{10}H_{19}O{\cdot}CH_2Ph$, is a colourless, viscid liquid, b. p. 194—196°/20 mm. Its *phenylurethane* melts at 153—154°. 2-*Benzylidene*-dl-iso*menthone*, $C_{10}H_{16}O{:}CHPh$, is a colourless liquid, b. p. 193—195°/15 mm. The corresponding *benzyl* compound, $C_{10}H_{17}O{\cdot}CH_2Ph$, is a colourless, viscid liquid, b. p. 195—197°/20 mm., d_4^{20} 0·9957, n_D^{20} 1·5230, and $[R_L]_D$ 74·92. 6-*Benzyl*-dl-iso*menthone*, $C_{10}H_{17}O{\cdot}CH_2Ph$, is a colourless, viscid liquid, b. p. 202—203°/14 mm., d_4^{20} 0·9884, n_D^{20} 1·5176, and $[R_L]_D$ 74·84. Its *semicarbazone* crystallises in colourless prisms, m. p. 170—171°. 6-Benzyl-*dl-iso*menthone distils at 213—220°/20 mm., and has d_4^{20} 0·9905, n_D^{20} 1·5239, and $[R_L]_D$ 75·42. Its *semicarbazone* has m. p. 170—171°. 6-*Benzyl*-2-*benzylidene*-dl-iso*menthone* is a yellow, mobile oil, b. p. 218—225°/15 mm. Reduction of this yields 2 : 6-*dibenzyl*-dl-iso*menthol*, a pale yellow, viscid liquid, b. p. 282—287°/23 mm. 6-*Benzyl*-dl-iso*menthol*, $C_{10}H_{19}O{\cdot}CH_2Ph$, distils at 203—207°/16 mm. Its *phenylurethane* crystallises in needles and

has m. p. 138—139°. A crystalline variety of the *iso*menthol, m. p. 66—68°, has also been obtained. F. G. P.

Higher Terpene Compounds. XVIII. The Constitution of Cadinene. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, **7**, 84—94).—The carbon framework of cadinene has already been established by its dehydrogenation with sulphur to cadaline (Ruzicka and Meyer, A., 1921, i, 573). This result has now been confirmed by the catalytic dehydrogenation of cadinene with platinum black in a high vacuum at 300°. It remains therefore to determine the positions of the two double bonds. That one of these is probably adjacent to the *iso*propyl group has already been shown (Ruzicka and Seidel, A., 1922, i, 562). It is now shown, by a variety of arguments, that cadinene is probably to be represented by one or both of the two annexed formulæ.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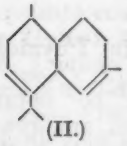
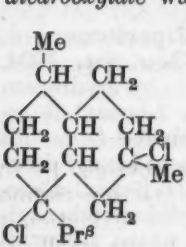
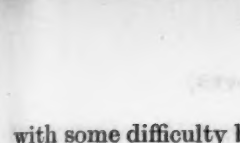

(II.)

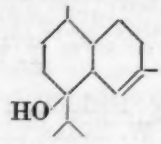
The products obtained by the action of ozone on cadinene, followed by decomposition of the ozonide first formed, render it extremely improbable that both double bonds are contained in the same ring. Although great difficulty was experienced in obtaining any identifiable products from this reaction, an *ethyl dicarboxylate* was obtained, b. p. 190—200°/0·2 mm., having the composition $C_{19}H_{30}O_5$ or $C_{19}H_{32}O_6$, in which all the carbon atoms of cadinene are intact. The absence of conjugated double bonds in cadinene is shown by the failure of attempts at reduction with sodium and amyl alcohol. The oxidation of cadinene with manganese dioxide and sulphuric acid as described by Ruzicka, Schinz, and Meyer (this vol., i, 171) resulted in the formation of trimellitic acid and mellophanic acid as primary products, and benzenepentacarboxylic acid as a secondary product. Cadinene dihydrochloride can be definitely stated to have the annexed formula. E. H. R.



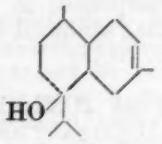
Higher Terpene Compounds. XIX. Cadinol from Galbanum Oil. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, **7**, 94—105).—A sesquiterpene alcohol, cadinol, $C_{15}H_{26}O$, which by loss of a molecule of water gives cadinene, was discovered by Semmler and Jonas in galbanum resin (A., 1915, i, 573). Having elucidated the constitution of cadinene (preceding abstract), the authors now attempt to discover that of cadinol. The compound does not react at a high temperature with phthalic anhydride, and must therefore be a tertiary alcohol. To determine the position of the double bond and of the hydroxyl group, the action of ozone was studied on cadinol itself and on the dihydrocadinene obtained by hydrogenating cadinol and then removing water. An attempt to reduce cadinol to a dihydrocadinene by heating with zinc dust was unsuccessful; only cadinene was obtained, by dehydration of the cadinol. Reduction of cadinol to *dihydrocadinol* was effected

with some difficulty by hydrogen and platinum black; it is a colourless oil, b. p. 150—153°/12 mm., $[\alpha]_D$ +23°, n_D^{16} 1·4948, d_4^{16} 0·9579. By boiling with 90% formic acid, dihydrocadinol is converted into *dihydrocadinene* (annexed formula), a colourless oil, b. p. 129—131°/12 mm., $[\alpha]_D$ +19·8°, n_D^{13} 1·4952, d_4^{13} 0·8999. By the action of ozone on this compound and decomposition of the ozonide there were obtained a keto-aldehyde and a keto-acid by the disruption of the hydrocarbon at the double bond; neither, however, was obtained in a pure condition. By ozonisation of cadinol itself there was obtained a neutral product, $C_{15}H_{24}O_2$, probably a *ketone-alcohol*, b. p. 180—184°/12 mm.; it contains one double bond. In addition a doubly unsaturated *ketone*, $C_{15}H_{22}O$, probably formed from the previous compound by loss of water, was obtained, b. p. 140—145°/12 mm. Oxidation of this ketone with manganese dioxide and sulphuric acid gave only mellophanic acid. The higher-boiling fractions of the neutral products from the ozonisation of cadinol gave, besides mellophanic acid, trimellitic acid. These observations can be explained on the assumption that cadinol consists of at least two forms, α and β, with probably a small proportion of a third form, γ, having the formulæ:

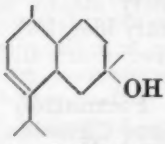




α-Cadinol.



β-Cadinol.



γ-Cadinol.

Structural formulæ are suggested for the products obtained by the ozonisation of cadinol, based on the above formulæ for cadinol. The cause of the formation of trimellitic acid by oxidation of higher fractions of these products is traced back to the small proportion of γ-cadinol probably present in the cadinol. E. H. R.

The Chlorohydrins of β-Pinene. G. G. Henderson and C. A. Kerr (*J. Chem. Soc.*, 1924, **125**, 102—106).—β-Pinene, on treatment with a very dilute aqueous solution of hypochlorous acid, gives mainly a mixture of three isomeric crystalline *dichlorohydrins*, $C_{10}H_{18}O_2Cl_2$, of m. p. 135°, 166°, and 131°, respectively. They are isomeric but not identical with the corresponding compounds prepared from α-pinene. The dichlorohydrin of m. p. 135° is converted into a *monochlorohydrin*, $C_{10}H_{17}O_2Cl$, m. p. 128—129°, by the action of dilute potassium hydroxide solution; this is an isomeride of pinol glycol chlorohydrin. Further action of caustic alkali converts it into an oily liquid which is apparently somewhat similar to pinol oxide in properties. The dichlorohydrin, m. p. 166°, also yields an oily liquid on treatment with caustic alkali, but a solid monochlorohydrin could not be obtained in this case. The third dichlorohydrin, m. p. 131°, is unaffected by caustic alkali in the cold. F. G. P.

Some Oxidation Products of β-Pinene. G. G. HENDERSON and D. CHISHOLM (*J. Chem. Soc.*, 1924, **125**, 107—113).—β-Pinene unites with chromyl chloride to form a solid *compound*, $C_{10}H_{16}{\cdot}2CrO_2Cl_2$, which on decomposition by water yields as chief product the ketone $C_9H_{14}O$, previously prepared in a similar fashion from α-pinene. A trace of an aldehyde and a small quantity of the inactive form of *trans*-pinol glycol were also obtained. Oxidation of β-pinene in glacial acetic acid solution by hydrogen peroxide gives a mixture of volatile and non-volatile products, the chief constituents of the volatile portion being borneol and a little fenchyl alcohol. The non-volatile portion could not be obtained sufficiently pure for identification. F. G. P.

Diacetyl Compound of Desmotropo-Artemisin. P. BERTOLO (*Gazzetta*, 1923, **53**, 867—869).—It is now found that desmotropo-artemisin forms a diacetyl derivative, so that, in the transformation of artemisin into desmotropo-artemisin, the fourth oxygen atom retains its alcoholic character (cf. A., 1923, i, 1108).

Diacetyldesmotropo-artemisin, $C_{19}H_{22}O_6$, crystallises in hard, lustrous, white needles, often grouped in radiating masses, m. p. 149—150°, $[\alpha]_D^{25}$ −50·75° (in alcohol). When hydrolysed by means of alcoholic potassium hydroxide, it yields, not artemisin, but a moderately stable, acid compound, m. p. above 200°, which is apparently identical with that obtained by hydrolysis of the acetyl derivative of artemisin (*loc. cit.*). T. H. P.

The Formation of Free Radicals by Reduction with Vanadous Chloride. J. B. CONANT and A. W. SLOAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2466—2472).—The addition of vanadous chloride solution to a solution of triphenylpyrylium chloride, or of its ferric chloride double salt, in the absence of air, causes the formation of a red precipitate, which is thought to be a *free radical*. With chloroform or benzene, it gives a red solution, the colour of which disappears when it is shaken with air. The substance is reoxidised to the pyrylium salt when it is treated in aqueous suspension with a solution of a ferric salt; if this process is conducted in the absence of oxygen, using freshly prepared material, a maximum of 1 mol. of ferric salt is required, but much less than this is needed if the compound, which is evidently unstable, has been kept for a few hours, even in an atmosphere of carbon dioxide.

The action of an excess of vanadous chloride on 9-phenylxanthylium chloride, in hydrochloric acid solution, in the absence of air, gives Gomberg and Cone's free radical, phenylxanthyl, which is identified by conversion into its peroxide.

Triphenylcarbinol, in concentrated hydrochloric acid or concentrated sulphuric acid solution, is reduced by means of vanadous chloride in an atmosphere of carbon dioxide to triphenylmethyl, which is likewise identified by means of the peroxide.

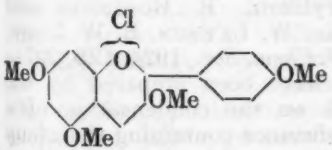
The action of vanadous chloride on a very dilute solution of xanthylium chloride in concentrated hydrochloric acid gives a pink solid, which may be kept for a few hours in air at the ordinary

temperature, but gradually changes to the colourless dixanthyl. Attempts to dry it in an atmosphere of nitrogen without loss of colour have been unsuccessful. When the bright pink solid is washed with water, drained, and dissolved in chloroform in an atmosphere of nitrogen, the solution is momentarily red; this colour disappears in the course of a few seconds. It is evident, from the last experiment, that polymerisation, and not oxidation, causes the change to dixanthyl. There is therefore strong evidence that the pink solid is the free radical, *xanthyl*.

The addition of vanadous chloride to an aqueous solution of benzylpyridinium chloride does not cause the formation of a precipitate, although the first portions of vanadous chloride undergo a change of colour; after making the solution alkaline, however, *N* : *N'*-dibenzyltetrahydrodipyridyl may be extracted from the solution by means of ether. W. S. N.

Chloro- and Amino-anthracoumarins. V. I. Minaev (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 680—684).—A short abstract of this work has already appeared (A., 1922, i, 162); the preparation of the following additional compounds is now described: 8-*aminoanthracoumarin*, from *m*-aminocinnamic and *m*-hydroxybenzoic acid, silvery crystals resembling β-naphthol, softens at 285°, carbonises at about 300°; 8-*chloroanthracoumarin*, obtained in a similar way from *m*-chlorocinnamic acid, forms brown crystals, m. p. 241°; gives on sublimation golden-yellow needles, m. p. 329°; 9-*aminoanthracoumarin*, obtained by condensing *p*-aminocinnamic acid and *m*-hydroxybenzoic acid, and the corresponding *chloro*-compound, were also prepared, but their properties are not recorded. G. A. R. K.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. III. A New Synthesis of Pelargonidin Chloride. D. D. Pratt and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 188—199).—Phloroglucinol dimethyl ether on treatment with formanilide and phosphoryl chloride, followed by subsequent decomposition, yields 2-hydroxy-4 : 6-dimethoxybenzaldehyde and a smaller relative amount of 4-hydroxy-2 : 6-dimethoxybenzaldehyde. When hydrogen chloride is passed into a cold solution of the 2-hydroxy-compound in the presence of ω-4-dimethoxyacetophenone, a good yield of tetramethylpelargonidin chloride (annexed formula) is obtained.

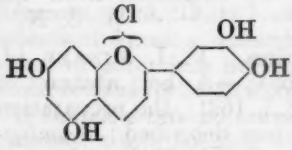


On demethylation, pelargonidin chloride is produced. 4-Hydroxy-2 : 6-dimethoxybenzaldehyde on similar treatment gives a trimethylpelargonidin chloride. It is suggested that the blue coloration characteristic of pelargonidin and other anthocyanidins is dependent on the presence of at least four hydroxyl groups, as well as on their positions. 3 : 7-*Dihydroxy*-2-*phenylbenzopyrylium chloride* crystallises in orange-brown prisms, decomposing at 184°. 3 : 7 : 4'-*Trihydroxy*-2-*phenylbenzopyrylium chloride*, $C_{15}H_{11}O_4Cl,H_2O$, crystallises

in needles, and decomposes at 262°. *4-Hydroxy-2 : 6-dimethoxybenzaldehyde* crystallises in colourless prisms, m. p. 190°. *Trimethylgalangidin ferrichloride* (*3 : 5 : 7-trimethoxy-2-phenylbenzopyrylium ferrichloride*) forms yellowish-brown prisms, m. p. 174°. The *trimethylgalangidin chloride* crystallises in orange-red needles.

F. G. P.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. IV. Flavylium Salts related to Chrysin, Apigenin, and Luteolin. D. D. PRATT, R. ROBINSON, and P. N. WILLIAMS (*J. Chem. Soc.*, 1924, **125**, 199—207; cf. previous abstract).—A series of compounds related to the flavones has been obtained and a system of nomenclature based on names suggesting their relationship to particular flavones and having the termination *-idin* suggested. Thus (I) is luteolidin chloride. The dimethyl ether of chrysinidin chloride is obtained by the action of hydrogen chloride on acetophenone in the presence of 2-hydroxy-4 : 6-dimethoxybenzaldehyde, and has been isolated as a ferrichloride. With phloroglucinol, *p*-anisyl β-hydroxyvinyl ketone reacts in the presence of hydrogen chloride to give acacetidin chloride (II). Trimethylapigenidin ferrichloride has been prepared from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and acetylanisole. *Dimethylchrysinidin ferrichloride*, $C_{17}H_{15}O_3Cl_4Fe$, crystallises in reddish-brown prisms, m. p. 178°. *p-Anisyl β-hydroxyvinyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$, can be isolated as a *copper* salt, green prisms, m. p. 206—207°. *7-Hydroxy-4′-methoxy-2-phenylbenzopyrylium chloride*, $C_{16}H_{13}O_3Cl,2H_2O$, brownish-orange needles, decomposes at 182—183°; its *picrate* melts at 219—221°. *Acacetidin chloride* forms brown prisms, m. p. >360°; *trimethylapigenidin ferrichloride*, orange needles; *2-hydroxy-4 : 6-dimethoxystyryl 3 : 4-dimethoxyphenyl ketone*, yellow prisms, m. p. 178—179°; *tetramethyl-luteolidin ferrichloride*, salmon-red needles, m. p. 206—207°.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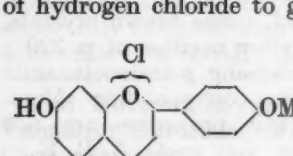
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F. G. P.

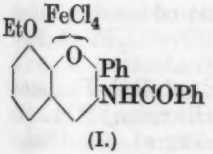
Some Derivatives of Benzopyrylium. R. ROBINSON and (in part) H. G. CRABTREE, C. R. DAS, W. LAWSON, R. W. LUNT, B. H. ROBERTS, and P. N. WILLIAMS (*J. Chem. Soc.*, 1924, **125**, 207—214).—The oxonium salts described have been prepared by the method of synthesis, which depends on the condensation of a derivative of salicylaldehyde and a substance containing the group $-CO{\cdot}CH_2-$, under the influence of hydrogen chloride. *4-Methoxyphenyl 2-hydroxy-5-methylstyryl ketone*,

$$OH{\cdot}C_6H_3Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

forms yellow plates, m. p. 151—152°; *4′-methoxy-2-phenyl-6-methyl-*

benzopyrylium ferrichloride, $C_{17}H_{15}O_2Cl_4Fe$, obtained from the ketone, crystallises in crimson needles, m. p. 165—166°. *Phenyl 2-hydroxy-3-methoxystyryl ketone*, $MeO{\cdot}C_6H_3(OH){\cdot}CH{:}CH{\cdot}COPh$, crystallises in yellow prisms, m. p. 112°. *8-Methoxy-2-phenylbenzopyrylium ferrichloride*, from the ketone, crystallises in reddish-brown needles, m. p. 157°. *8 : 4′-Dimethoxy-2-phenylbenzopyrylium ferrichloride*, obtained from *o*-vanillin and *p*-methoxyacetophenone, crystallises in brown needles, m. p. 180°. *2 : 3 : 4-Trimethoxyphenyl 2-hydroxy-3-methoxystyryl ketone*, obtained from *o*-vanillin and gallacetophenone trimethyl ether, forms bright yellow needles, m. p. 145°. *2′-Hydroxy-8 : 3′ : 4′-trimethoxy-2-phenylbenzopyrylium ferrichloride* forms dark red needles, m. p. 194°; the *picrate*, red prisms, m. p. 164°; the *periodide*, purple needles, m. p. 133°; the *mercurichloride*, yellow needles, m. p. 143°. *2-Phenyl-3 : 4′-dimethylbenzopyrylium ferrichloride*, from salicylaldehyde and *p*-tolyl ethyl ketone, forms yellow needles, m. p. 165—166°. *8-Methoxy-2-phenyl-3 : 4′-dimethylbenzopyrylium ferrichloride* from *o*-vanillin and *p*-tolyl ethyl ketone, forms orange-brown needles, m. p. 172°; *8-methoxy-2-α-naphthylbenzopyrylium ferrichloride*, from *o*-vanillin and α-naphthyl methyl ketone, brownish-red needles, m. p. 230°; *2′-hydroxy-3′-methoxy-2-benzylidene-1-hydrindone*, from *o*-vanillin and α-hydrindone, yellow needles, m. p. 198°; *8-methoxy-2 : 3-indeno-(1 : 2)-benzopyrylium ferrichloride*, red needles, m. p. 187—188°. F. G. P.

Some Benzopyrylium Salts. L. R. RIDGWAY and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 214—222).—Attempts to prepare a benzopyrylium salt in which a halogen atom occurs in position 3 have not so far succeeded. The attachment of nitrogen to the pyrylium nucleus has been successful, and 3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride (I) has been prepared from 2-hydroxy-3-ethoxybenzaldehyde and ω-benzoylaminoacetophenone. The removal of the benzoyl group from this salt was not possible. An account is included of some compounds which have been prepared in order to throw light on the property of fluorescence in relation to structure in this group. *8-Ethoxy-2-phenylbenzopyrylium ferrichloride*, $C_{17}H_{15}O_2Cl_4Fe$, forms brown plates, m. p. 139—140°; *3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride* (I), orange-red needles, m. p. 198°; *3-benzoylamino-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride*, $C_{25}H_{22}O_4NCl_4Fe$, reddish-brown plates, m. p. 201°. *5-Ethoxy-4-(2-hydroxy-3-ethoxybenzylidene)-1 : 2 : 3 : 4-tetrahydroxanthylium ferrichloride* (II) is obtained from cyclohexanone and 2-hydroxy-3-ethoxybenzaldehyde. It is a chocolate-coloured powder, m. p. 197°. The chloride obtained from this when boiled with water containing a



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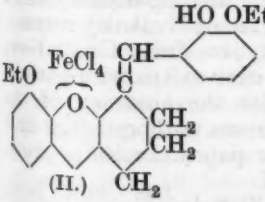
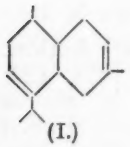


(II.)

has m. p. 138—139°. A crystalline variety of the *iso*menthol, m. p. 66—68°, has also been obtained. F. G. P.

Higher Terpene Compounds. XVIII. The Constitution of Cadinene. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, **7**, 84—94).—The carbon framework of cadinene has already been established by its dehydrogenation with sulphur to cadaline (Ruzicka and Meyer, A., 1921, i, 573). This result has now been confirmed by the catalytic dehydrogenation of cadinene with platinum black in a high vacuum at 300°. It remains therefore to determine the positions of the two double bonds. That one of these is probably adjacent to the *iso*propyl group has already been shown (Ruzicka and Seidel, A., 1922, i, 562). It is now shown, by a variety of arguments, that cadinene is probably to be represented by one or both of the two annexed formulæ.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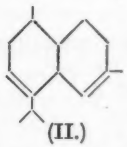
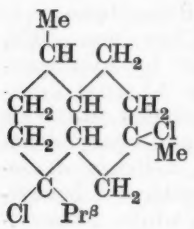
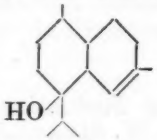

(II.)

The products obtained by the action of ozone on cadinene, followed by decomposition of the ozonide first formed, render it extremely improbable that both double bonds are contained in the same ring. Although great difficulty was experienced in obtaining any identifiable products from this reaction, an *ethyl dicarboxylate* was obtained, b. p. 190—200°/0·2 mm., having the composition $C_{19}H_{30}O_5$ or $C_{19}H_{32}O_6$, in which all the carbon atoms of cadinene are intact. The absence of conjugated double bonds in cadinene is shown by the failure of attempts at reduction with sodium and amyl alcohol. The oxidation of cadinene with manganese dioxide and sulphuric acid as described by Ruzicka, Schinz, and Meyer (this vol., i, 171) resulted in the formation of trimellitic acid and mellophanic acid as primary products, and benzenepentacarboxylic acid as a secondary product. Cadinene dihydrochloride can be definitely stated to have the annexed formula. E. H. R.

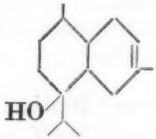


Higher Terpene Compounds. XIX. Cadinol from Galbanum Oil. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, **7**, 94—105).—A sesquiterpene alcohol, cadinol, $C_{15}H_{26}O$, which by loss of a molecule of water gives cadinene, was discovered by Semmler and Jonas in galbanum resin (A., 1915, i, 573). Having elucidated the constitution of cadinene (preceding abstract), the authors now attempt to discover that of cadinol. The compound does not react at a high temperature with phthalic anhydride, and must therefore be a tertiary alcohol. To determine the position of the double bond and of the hydroxyl group, the action of ozone was studied on cadinol itself and on the dihydrocadinene obtained by hydrogenating cadinol and then removing water. An attempt to reduce cadinol to a dihydrocadinene by heating with zinc dust was unsuccessful; only cadinene was obtained, by dehydration of the cadinol. Reduction of cadinol to *dihydrocadinol* was effected

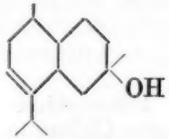
with some difficulty by hydrogen and platinum black; it is a colourless oil, b. p. 150—153°/12 mm., $[\alpha]_D$ +23°, n_D^{16} 1·4948, d_4^{16} 0·9579. By boiling with 90% formic acid, dihydrocadinol is converted into *dihydrocadinene* (annexed formula), a colourless oil, b. p. 129—131°/12 mm., $[\alpha]_D$ +19·8°, n_D^{13} 1·4952, d_4^{13} 0·8999. By the action of ozone on this compound and decomposition of the ozonide there were obtained a keto-aldehyde and a keto-acid by the disruption of the hydrocarbon at the double bond; neither, however, was obtained in a pure condition. By ozonisation of cadinol itself there was obtained a neutral product, $C_{15}H_{24}O_2$, probably a *ketone-alcohol*, b. p. 180—184°/12 mm.; it contains one double bond. In addition a doubly unsaturated *ketone*, $C_{15}H_{22}O$, probably formed from the previous compound by loss of water, was obtained, b. p. 140—145°/12 mm. Oxidation of this ketone with manganese dioxide and sulphuric acid gave only mellophanic acid. The higher-boiling fractions of the neutral products from the ozonisation of cadinol gave, besides mellophanic acid, trimellitic acid. These observations can be explained on the assumption that cadinol consists of at least two forms, α and β, with probably a small proportion of a third form, γ, having the formulæ:



α-Cadinol.



β-Cadinol.



γ-Cadinol.

Structural formulæ are suggested for the products obtained by the ozonisation of cadinol, based on the above formulæ for cadinol. The cause of the formation of trimellitic acid by oxidation of higher fractions of these products is traced back to the small proportion of γ-cadinol probably present in the cadinol. E. H. R.

The Chlorohydrins of β-Pinene. G. G. Henderson and C. A. Kerr (*J. Chem. Soc.*, 1924, **125**, 102—106).—β-Pinene, on treatment with a very dilute aqueous solution of hypochlorous acid, gives mainly a mixture of three isomeric crystalline *dichlorohydrins*, $C_{10}H_{18}O_2Cl_2$, of m. p. 135°, 166°, and 131°, respectively. They are isomeric but not identical with the corresponding compounds prepared from α-pinene. The dichlorohydrin of m. p. 135° is converted into a *monochlorohydrin*, $C_{10}H_{17}O_2Cl$, m. p. 128—129°, by the action of dilute potassium hydroxide solution; this is an isomeride of pinol glycol chlorohydrin. Further action of caustic alkali converts it into an oily liquid which is apparently somewhat similar to pinol oxide in properties. The dichlorohydrin, m. p. 166°, also yields an oily liquid on treatment with caustic alkali, but a solid monochlorohydrin could not be obtained in this case. The third dichlorohydrin, m. p. 131°, is unaffected by caustic alkali in the cold. F. G. P.

Some Oxidation Products of β-Pinene. G. G. HENDERSON and D. CHISHOLM (*J. Chem. Soc.*, 1924, **125**, 107—113).—β-Pinene unites with chromyl chloride to form a solid *compound*, $C_{10}H_{16}{\cdot}2CrO_2Cl_2$, which on decomposition by water yields as chief product the ketone $C_9H_{14}O$, previously prepared in a similar fashion from α-pinene. A trace of an aldehyde and a small quantity of the inactive form of *trans*-pinol glycol were also obtained. Oxidation of β-pinene in glacial acetic acid solution by hydrogen peroxide gives a mixture of volatile and non-volatile products, the chief constituents of the volatile portion being borneol and a little fenchyl alcohol. The non-volatile portion could not be obtained sufficiently pure for identification. F. G. P.

Diacetyl Compound of Desmotropo-Artemisin. P. BERTOLO (*Gazzetta*, 1923, **53**, 867—869).—It is now found that desmotropo-artemisin forms a diacetyl derivative, so that, in the transformation of artemisin into desmotropo-artemisin, the fourth oxygen atom retains its alcoholic character (cf. A., 1923, i, 1108).

Diacetyldesmotropo-artemisin, $C_{19}H_{22}O_6$, crystallises in hard, lustrous, white needles, often grouped in radiating masses, m. p. 149—150°, $[\alpha]_D^{25}$ −50·75° (in alcohol). When hydrolysed by means of alcoholic potassium hydroxide, it yields, not artemisin, but a moderately stable, acid compound, m. p. above 200°, which is apparently identical with that obtained by hydrolysis of the acetyl derivative of artemisin (*loc. cit.*). T. H. P.

The Formation of "Free" Radicals by Reduction with Vanadous Chloride. J. B. CONANT and A. W. SLOAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2466—2472).—The addition of vanadous chloride solution to a solution of triphenylpyrylium chloride, or of its ferric chloride double salt, in the absence of air, causes the formation of a red precipitate, which is thought to be a *free radical*. With chloroform or benzene, it gives a red solution, the colour of which disappears when it is shaken with air. The substance is reoxidised to the pyrylium salt when it is treated in aqueous suspension with a solution of a ferric salt; if this process is conducted in the absence of oxygen, using freshly prepared material, a maximum of 1 mol. of ferric salt is required, but much less than this is needed if the compound, which is evidently unstable, has been kept for a few hours, even in an atmosphere of carbon dioxide.

The action of an excess of vanadous chloride on 9-phenylxanthylium chloride, in hydrochloric acid solution, in the absence of air, gives Gomberg and Cone's free radical, phenylxanthyl, which is identified by conversion into its peroxide.

Triphenylcarbinol, in concentrated hydrochloric acid or concentrated sulphuric acid solution, is reduced by means of vanadous chloride in an atmosphere of carbon dioxide to triphenylmethyl, which is likewise identified by means of the peroxide.

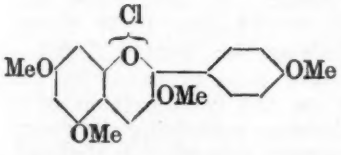
The action of vanadous chloride on a very dilute solution of xanthylium chloride in concentrated hydrochloric acid gives a pink solid, which may be kept for a few hours in air at the ordinary

temperature, but gradually changes to the colourless dixanthyl. Attempts to dry it in an atmosphere of nitrogen without loss of colour have been unsuccessful. When the bright pink solid is washed with water, drained, and dissolved in chloroform in an atmosphere of nitrogen, the solution is momentarily red; this colour disappears in the course of a few seconds. It is evident, from the last experiment, that polymerisation, and not oxidation, causes the change to dixanthyl. There is therefore strong evidence that the pink solid is the free radical, *xanthyl*.

The addition of vanadous chloride to an aqueous solution of benzylpyridinium chloride does not cause the formation of a precipitate, although the first portions of vanadous chloride undergo a change of colour; after making the solution alkaline, however, *N* : *N'*-dibenzyltetrahydrodipyridyl may be extracted from the solution by means of ether. W. S. N.

Chloro- and Amino-anthracoumarins. V. I. Minaev (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 680—684).—A short abstract of this work has already appeared (A., 1922, i, 162); the preparation of the following additional compounds is now described: 8-*aminoanthracoumarin*, from *m*-aminocinnamic and *m*-hydroxybenzoic acid, silvery crystals resembling β-naphthol, softens at 285°, carbonises at about 300°; 8-*chloroanthracoumarin*, obtained in a similar way from *m*-chlorocinnamic acid, forms brown crystals, m. p. 241°; gives on sublimation golden-yellow needles, m. p. 329°; 9-*aminoanthracoumarin*, obtained by condensing *p*-aminocinnamic acid and *m*-hydroxybenzoic acid, and the corresponding *chloro*-compound, were also prepared, but their properties are not recorded. G. A. R. K.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. III. A New Synthesis of Pelargonidin Chloride. D. D. Pratt and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 188—199).—Phloroglucinol dimethyl ether on treatment with formanilide and phosphoryl chloride, followed by subsequent decomposition, yields 2-hydroxy-4 : 6-dimethoxybenzaldehyde and a smaller relative amount of 4-hydroxy-2 : 6-dimethoxybenzaldehyde. When hydrogen chloride is passed into a cold solution of the 2-hydroxy-compound in the presence of ω-4-dimethoxyacetophenone, a good yield of tetramethylpelargonidin chloride (annexed formula) is obtained.

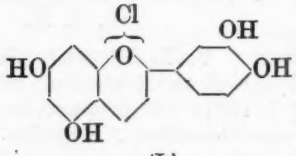


On demethylation, pelargonidin chloride is produced. 4-Hydroxy-2 : 6-dimethoxybenzaldehyde on similar treatment gives a trimethylpelargonidin chloride. It is suggested that the blue coloration characteristic of pelargonidin and other anthocyanidins is dependent on the presence of at least four hydroxyl groups, as well as on their positions. 3 : 7-*Dihydroxy-2-phenylbenzopyrylium chloride* crystallises in orange-brown prisms, decomposing at 184°. 3 : 7 : 4'-*Trihydroxy-2-phenylbenzopyrylium chloride*, $C_{15}H_{11}O_4Cl,H_2O$, crystallises

in needles, and decomposes at 262°. 4-*Hydroxy*-2 : 6-*dimethoxybenzaldehyde* crystallises in colourless prisms, m. p. 190°. *Trimethylgalangidin ferrichloride* (3 : 5 : 7-*trimethoxy*-2-*phenylbenzopyrylium ferrichloride*) forms yellowish-brown prisms, m. p. 174°. The *trimethylgalangidin chloride* crystallises in orange-red needles.

F. G. P.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. IV. Flavylium Salts related to Chrysin, Apigenin, and Luteolin. D. D. PRATT, R. ROBINSON, and P. N. WILLIAMS (*J. Chem. Soc.*, 1924, **125**, 199—207; cf. previous abstract).—A series of compounds related to the flavones has been obtained and a system of nomenclature based on names suggesting their relationship to particular flavones and having the termination *-idin* suggested. Thus (I) is luteolidin chloride. The dimethyl ether of chrysinidin chloride is obtained by the action of hydrogen chloride on acetophenone in the presence of 2-hydroxy-4 : 6-dimethoxybenzaldehyde, and has been isolated as a ferrichloride. With phloroglucinol, *p*-anisyl β-hydroxyvinyl ketone reacts in the presence of hydrogen chloride to give acacetidin chloride (II). Trimethylapigenidin ferrichloride has been prepared from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and acetylanisole. *Dimethylchrysinidin ferrichloride*, $C_{17}H_{15}O_3Cl_4Fe$, crystallises in reddish-brown prisms, m. p. 178°. p-*Anisyl* β-*hydroxyvinyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$, can be isolated as a *copper* salt, green prisms, m. p. 206—207°. 7-*Hydroxy*-4′-*methoxy*-2-*phenylbenzopyrylium chloride*, $C_{16}H_{13}O_3Cl,2H_2O$, brownish-orange needles, decomposes at 182—183°; its *picrate* melts at 219—221°. *Acacetidin chloride* forms brown prisms, m. p. >360°; *trimethylapigenidin ferrichloride*, orange needles; 2-*hydroxy*-4 : 6-*dimethoxystyryl* 3 : 4-*dimethoxyphenyl ketone*, yellow prisms, m. p. 178—179°; *tetramethyl-luteolidin ferrichloride*, salmon-red needles, m. p. 206—207°.



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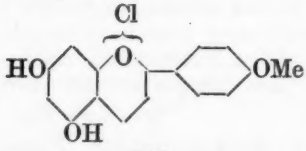

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F. G. P.

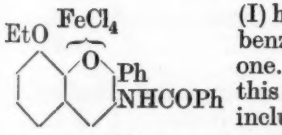
Some Derivatives of Benzopyrylium. R. ROBINSON and (in part) H. G. CRABTREE, C. R. DAS, W. LAWSON, R. W. LUNT, B. H. ROBERTS, and P. N. WILLIAMS (*J. Chem. Soc.*, 1924, **125**, 207—214).—The oxonium salts described have been prepared by the method of synthesis, which depends on the condensation of a derivative of salicylaldehyde and a substance containing the group $-CO{\cdot}CH_2-$, under the influence of hydrogen chloride. 4-*Methoxyphenyl* 2-*hydroxy*-5-*methylstyryl ketone*,

$$OH{\cdot}C_6H_3Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

forms yellow plates, m. p. 151—152°; 4′-*methoxy*-2-*phenyl*-6-*methyl*-

benzopyrylium ferrichloride, $C_{17}H_{15}O_2Cl_4Fe$, obtained from the ketone, crystallises in crimson needles, m. p. 165—166°. *Phenyl 2-hydroxy-3-methoxystyryl ketone*, $MeO{\cdot}C_6H_3(OH){\cdot}CH{:}CH{\cdot}COPh$, crystallises in yellow prisms, m. p. 112°. *8-Methoxy-2-phenylbenzopyrylium ferrichloride*, from the ketone, crystallises in reddish-brown needles, m. p. 157°. *8 : 4'-Dimethoxy-2-phenylbenzopyrylium ferrichloride*, obtained from *o*-vanillin and *p*-methoxyacetophenone, crystallises in brown needles, m. p. 180°. *2 : 3 : 4-Trimethoxyphenyl 2-hydroxy-3-methoxystyryl ketone*, obtained from *o*-vanillin and gallacetophenone trimethyl ether, forms bright yellow needles, m. p. 145°. *2'-Hydroxy-8 : 3' : 4'-trimethoxy-2-phenylbenzopyrylium ferrichloride* forms dark red needles, m. p. 194°; the *picrate*, red prisms, m. p. 164°; the *periodide*, purple needles, m. p. 133°; the *mercurichloride*, yellow needles, m. p. 143°. *2-Phenyl-3 : 4'-dimethylbenzopyrylium ferrichloride*, from salicylaldehyde and *p*-tolyl ethyl ketone, forms yellow needles, m. p. 165—166°. *8-Methoxy-2-phenyl-3 : 4'-dimethylbenzopyrylium ferrichloride* from *o*-vanillin and *p*-tolyl ethyl ketone, forms orange-brown needles, m. p. 172°; *8-methoxy-2-α-naphthylbenzopyrylium ferrichloride*, from *o*-vanillin and α-naphthyl methyl ketone, brownish-red needles, m. p. 230°; *2'-hydroxy-3'-methoxy-2-benzylidene-1-hydrindone*, from *o*-vanillin and α-hydrindone, yellow needles, m. p. 198°; *8-methoxy-2 : 3-indeno-(1 : 2)-benzopyrylium ferrichloride*, red needles, m. p. 187—188°. F. G. P.

Some Benzopyrylium Salts. L. R. RIDGWAY and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 214—222).—Attempts to prepare a benzopyrylium salt in which a halogen atom occurs in position 3 have not so far succeeded. The attachment of nitrogen to the pyrylium nucleus has been successful, and 3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride (I) has been prepared from 2-hydroxy-3-ethoxybenzaldehyde and ω-benzoylaminoacetophenone. The removal of the benzoyl group from this salt was not possible. An account is included of some compounds which have been prepared in order to throw light on the property of fluorescence in relation to structure in this group. *8-Ethoxy-2-phenylbenzopyrylium ferrichloride*, $C_{17}H_{15}O_2Cl_4Fe$, forms brown plates, m. p. 139—140°; *3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride* (I), orange-red needles, m. p. 198°; *3-benzoylamino-4'-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride*, $C_{25}H_{22}O_4NCl_4Fe$, reddish-brown plates, m. p. 201°. *5-Ethoxy-4-(2-hydroxy-3-ethoxybenzylidene)-1 : 2 : 3 : 4-tetrahydroxanthylium ferrichloride* (II) is obtained from cyclohexanone and 2-hydroxy-3-ethoxybenzaldehyde. It is a chocolate-coloured powder, m. p. 197°. The chloride obtained from this when boiled with water containing a



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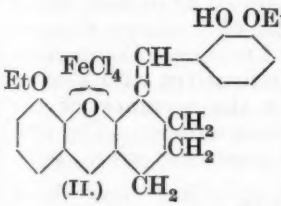
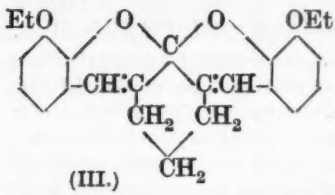
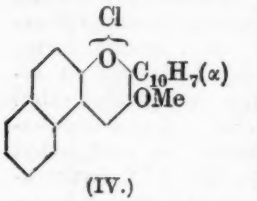


(II.)

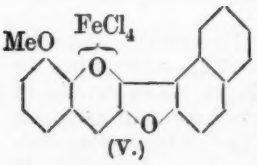
little hydrochloric acid is converted into *diethoxytrimethylenedibenzospiropyran* (III), colourless needles, m. p. 155°. *α-Naphthylmethoxymethyl ketone*, $C_{10}H_7\cdot CO\cdot CH_2\cdot OMe$, is obtained from methoxyacetonitrile and magnesium α-naphthyl bromide. It is a pale yellow, viscid oil, b. p. 184—186°/13 mm. It condenses with 2-hydroxy-5-methylbenzaldehyde to *3-methoxy-2-α-naphthyl-6-methylbenzopyrylium chloride*, $C_{21}H_{17}O_2Cl,3H_2O$, orange needles, m. p. 84°. The *ferrichloride* crystallises in plates, m. p. 184°. With 2-hydroxy-3-ethoxybenzaldehyde the above ketone yields *3-methoxy-8-ethoxy-2-α-naphthylbenzopyrylium chloride*, $C_{22}H_{18}O_3Cl,2H_2O$, orange-red plates, m. p. 115—116°, whilst with β-hydroxy-α-naphthaldehyde, *3-methoxy-2-α-naphthylnaphtha-(2 : 1)-pyrylium chloride* (IV) is obtained in red, microscopic plates, m. p. 94°. The *ferrichloride* forms bright red plates, m. p. 183°. *6 : 4′-Dimethoxy-2-phenylbenzopyrylium chloride* forms orange-red plates, m. p. 135°; the *ferrichloride* crystallises in brownish-red plates, m. p. 192—193°. *8-Methoxy-β-naphthacoumarono-(β : α-2 : 3)-benzopyrylium chloride* (V) is prepared from *o*-vanillin and β-naphthacoumaranone. It crystallises in green prisms, m. p. 236—240°. When warmed with ethyl alcohol and a trace of sodium acetate, it is decolorised and the colourless *ethyl ether* of the pyranol is obtained in the form of needles, m. p. 165°.



(III.)



(IV.)



(V.)

F. G. P.

"Tervalent" Carbon. I. The Tetra-arylallyl Radicals and their Derivatives. K. Ziegler [with G. Bremer, F. Thiel, and F. Thielmann] (*Annalen*, 1923, **434**, 34—78; cf. A., 1922, i, 1047).—This investigation was undertaken to determine the factors responsible for the dissociation of poly-substituted ethane derivatives. For this purpose, compounds of the type of octaphenyldiallyl were studied. Assuming that the theoretical considerations developed by Thiele and Werner are correct, the unsaturated ββ-diphenylvinyl group would possess a markedly higher degree of "valency requirement" than the relatively saturated phenyl residue. Comparison of the dissociation capacity of the diallyl derivatives with that of the hexaphenylethanes provides a test for the accuracy of the theoretical considerations advanced by various authors. The first results of the work are given in an earlier paper (*loc. cit.*). *9-ββ-Diphenylvinylxanthenol*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C<\begin{matrix}OH\\CH:CPh_2\end{matrix}$, has now been obtained in needles which on heating lose water and pass into the allene derivative. Characteristic salts are obtained, particularly

the *perchlorate*, as well as acid halogenides such as the *chloride-hydrochloride*, $O<^{C_6H_4}_{C_6H_4}>C(Cl,HCl)\cdot CH{:}CPh_2$, red needles, m. p. 156—157°, and the *bromide hydrobromide*, m. p. 130—131°; perhalogenides, namely, the *chloride tetrabromide* and *bromide tetrabromide*, reddish-brown powders, decomp. 123—124°, and 128—129°, respectively. Double salts of the xanthyl chloride are obtained by addition of heavy metal salts to solutions of the chloride hydrochloride in glacial acetic acid. The *zinc chloride* salt is a red, crystalline solid, decomposing at 165—166°. Hydrolysis of the salts regenerates the xanthenol, whilst tertiary amines such as pyridine and dimethylaniline convert them into the allene derivatives. Methyl and ethyl alcohols convert the hydrohalogenides into 9-*methoxy*- and 9-*ethoxy*-9-ββ-*diphenylvinylxanthen*, crystallising in needles, m. p. 133—134° and 136—137°, respectively. These ethers are readily decomposed by acids into alcohol and the coloured salts. The salts, particularly the chloride hydrochloride, dissolve in saturated alcoholic hydrogen chloride unaltered, and on reduction by zinc the parent substance, 9-ββ-*diphenylvinylxanthen*, has been obtained in large, colourless crystals, m. p. 164—165°. This has also been obtained from 9-xanthylacetic acid by the Grignard reaction. Aryl and alkyl derivatives of 9-ββ-diphenylvinylxanthen are obtained by the action of the Grignard reagent on the xanthyl salts, particularly on the perchlorate. The xanthen and its alkyl and aryl derivatives are easily reduced by hydriodic acid, the ββ-diphenylvinyl group probably being eliminated as αα-diphenylethane. 9-*Ethyl*-9-ββ-*diphenylvinylxanthen* crystallises in colourless crusts, m. p. 129—130°. These xanthens, when acted on by bromine, yield perbromides such as $O<^{C_6H_4}_{C_6H_4}>C(Br\cdot Br_x)H$, and brominated compounds of the type of αββ-*tribromo*-αα-*diphenylethane*, $Ph_2CBr\cdot CHBr_2$, m. p. 88—89°. Di-*p*-anisyl ketone and 2 : 4 : 4′-trimethoxybenzophenone, on treatment with the magnesium compound of ββ-diphenylvinyl bromide, yield alcohols, $(MeO\cdot C_6H_4)_2CR\cdot CH{:}CPh_2$ and $(MeO)_2C_6H_3(MeO\cdot C_6H_4)\cdot CR\cdot CH{:}CPh_2$, from which crystalline perchlorates may be prepared. The *trimethoxy*-compound forms fine red crystals yielding violet-red solutions. Pyridine converts it into 2 : 4 : 4′-trimethoxydiphenyl-γγ-diphenylallene, $(MeO)_2C_6H_3\cdot C(C_6H_4OMe){:}C{:}CPh_2$, colourless crystals, m. p. 134—135°. Tetraphenylpropene derivatives have been prepared, *ααγγ-tetraphenylallyl ethyl ether*, $Ph_2C(OEt)\cdot CH{:}CPh_2$, resulting from the action of alcoholic sulphuric acid on the corresponding alcohol. It forms colourless crystals, m. p. 106—107°. *Tetraphenylallyl perchlorate*, obtained from tetraphenylallyl alcohol, is an unstable, chocolate-brown powder, decomposing at 63—64°. On keeping, it is converted into the colourless 1 : 1 : 3-triphenylindene. Results show that the coloured compounds of the substituted tetra-allylallenes are true tetra-arylallyl salts, that tetra-arylallyl alcohols are pseudo-bases; the chlorides were not isolated, losing hydrogen chloride and giving tetra-allylallenes; these allenes readily add acid so as to form salts. Magnesium aryl

haloids convert the xanthen perchlorate into the free *di*-9-ββ-*diphenylvinylxanthyl*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C\cdot CH{:}CPh_2$, a colourless, crystalline powder, m. p. 144—145°, sparingly soluble in most reagents. This dissolves in benzene with a yellow colour, the solution becoming brown on warming, turning yellow again on cooling. Air completely decolorises the solution, a peroxide,

$$\left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(O-)\cdot CH{:}CPh_2\right]_2,$$

being obtained. Bromine converts the coloured solution into 9-ββ-diphenylvinylxanthyl bromide tetrabromide. Hydrazobenzene reduces it to 9-ββ-diphenylvinylxanthen (cf. triphenylmethyl). Sodium and potassium give coloured metal derivatives, the potassium derivative crystallising in the form of a copper-red sludge. Dry air decolorises the solutions of the alkali metal derivatives, water also decomposes them with production of the xanthen, whilst ethyl bromide converts them into the ethylxanthene. Tetraphenylhydrazine converts the free radical into 9-ββ-*diphenylvinylxanthyldiphenylamine*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(NPh_2)\cdot CH{:}CPh_2$, crystallising in colourless plates, m. p. 194—196° (cf. triphenylmethyl). These analogies with hexaphenylethane show that the xanthyl compound in solution exhibits radical dissociation. Molecular-weight determinations in naphthalene show that the xanthyl is decomposed to the extent of about 60% into 2 mols. of radical-like form. The free tetra-arylallyl radicals are also obtained by the decomposition of the corresponding perchlorates with the Grignard reagent. *Dianisyldiphenylallyl*, $(MeO\cdot C_6H_4)_2\cdot C\cdot CH{:}CPh_2$, crystallises in dark green plates, 2 : 4 : 4′-*trimethoxydiphenyl*-γγ-*diphenylallyl*,

$$(MeO)_2\cdot C_6H_3\cdot C(C_6H_4OMe)\cdot C\cdot CH{:}CPh_2,$$

is similar, but the colour is deeper. αα'γγ'-*Tetraphenylallyl*, the parent substance, is a green, crystalline powder, molecular-weight determinations in benzene showing a degree of dissociation of 80%. These three compounds are exceedingly stable. The corresponding peroxides are very unstable. The sodium compounds of the allyl radicals are readily converted into the corresponding propenes. In the triarylmethyl series, the union of the two benzene nuclei through oxygen opposes the association of the radicals, for 9-phenylxanthyl in naphthalene is present to the extent of about 50—70% in the unimolecular form and about 30—50% in the bimolecular form, whilst hexaphenylethane under like conditions is only dissociated to the extent of 15—25%. Tetraphenylallyl, on the other hand, in benzene solution at 4°, is present in the bimolecular form to the extent of at most 20%, whilst 9-ββ-diphenylvinylxanthyl in naphthalene at 80° is present perhaps to the extent of 40%; at 4°, therefore, it is still more strongly associated. If, according to Thiele and Werner, the high valency requirement of a residue is explained by its unsaturated character, based on the principle of a distribution of affinity, the existence of tetra-arylallyl radicals is a weighty argument in favour of this principle. αα-Diphenylethylene is essentially more unsaturated than benzene, so that it must be

assumed that the ββ-diphenylvinyl residue requires more valency than the phenyl residue, and in agreement with this it is found that on replacing two phenyl residues in hexaphenylethane by two such residues the tendency to dissociate is very much increased.
F. G. P.

Atropine Phosphates. L. DEBUCQUET (*J. Pharm. Chim.*, 1924, **29**, 15—22).—The salt $C_{17}H_{23}O_3N,H_3PO_4$ is obtained in 92% yield when an alcoholic solution containing equimolecular quantities of atropine and phosphoric acid is heated for half an hour in a water-bath at 90—95°, and then left to crystallise. Small, lustrous crystals (m. p. 196°) are obtained which are soluble in rather less than five times their weight of water (giving a solution acid to litmus), sparingly soluble in cold alcohol and almost insoluble in ether and chloroform. Attempts to prepare the salt, $(C_{17}H_{23}O_3N)_2,H_3PO_4$, gave only the monobasic phosphate (in diminished yield) and unchanged atropine. W. T. K. B.

Stereoisomerism and Local Anæsthetic Action in the β-Eucaine Group. Resolution of β- and *iso*-β-Eucaine. H. KING (*J. Chem. Soc.*, 1924, **125**, 41—57).—On benzoylation, α- and β-vinyldiacetonalkamines yield *O*-benzoyl derivatives and for convenience the name of *iso*-β-eucaine is proposed for the derivative of the β-compound. β-Eucaine has been resolved by means of camphorsulphonic acid. With *d*-camphor-10-sulphonic acid, the partial racemate, dl-β-*eucaine* d-*camphor*-10-*sulphonate*, was obtained, working between the ordinary temperature and zero, and it has been found possible to resolve this salt by means of the more soluble active forms which are unstable in respect of the partial racemate, a total yield of 54% of l-β-*eucaine* d-*camphorsulphonate* being obtained. Owing to the formation of a continuous series of mixed crystals between the two active salts, the more soluble *d*-β-eucaine *d*-camphorsulphonate could not be isolated, but the isolation of d-β-*eucaine* l-*camphorsulphonate* was finally accomplished by the use of *l*-camphor-10-sulphonic acid. *iso*-β-Eucaine was resolved by the use of *d*-α-bromocamphor-π-sulphonic acid. In this case the salts, being of approximately equal solubility, separate alternately from the solution on fractional crystallisation. On the rabbit's cornea *r*-β-eucaine, *r*-*iso*-β-eucaine and their optically active components have approximately equal local anæsthetic action; on the sciatic nerve of the frog, however, β-eucaine is a more powerful anæsthetic than *iso*-β-eucaine. dl-β-*Eucaine* d-*camphorate* forms plates, m. p. 211—212°; the l-*malate* has m. p. 212—213° and $[\alpha]_D$ −2·6°; the d-*tartrate* crystallises in tablets which have m. p. 257° and $[\alpha]_D$ +10·1°. The *d*-camphor-10-sulphonate (mono-alcoholate) forms tablets, m. p. 228—229°, $[\alpha]_D$ +10·3° (anhydrous salt). *l*-β-Eucaine *d*-camphorsulphonate forms leaflets, m. p. 248—249°, $[\alpha]_D$ 4·78° and 4·83°, whence the *l*-β-eucainium-ion has $[\alpha]_D$ −11°. *d*-β-Eucaine *l*-camphorsulphonate has $[\alpha]_D$ −5·09°, whence the *d*-β-eucainium-ion has $[\alpha]_D$ +10·6°. l-β-*Eucaine* forms prisms, m. p. 57—58°. The *hydrochloride* forms

plates (m. p. 244—245°, $[\alpha]_D$ −11·3°), the *picrate* (small prisms) having m. p. 198—199°. d-β-*Eucaine* has m. p. 57—58°, the *hydrochloride* having $[\alpha]_D$ +11·5°. r-β-*Eucaine hydrochloride* forms tablets, m. p. 277—279°; the free *base* has m. p. 70—71°; the *picrate* (plates), has m. p. 230·5—231·5°. d-α-*Vinyldiacetonalkamine hydrochloride* (tablets, m. p. above 300°), has $[\alpha]_D$ +13·3°; the l-*hydrochloride* has m. p. above 300° and $[\alpha]_{5461}$ −18·5°. The l-*base* forms prisms, m. p. 79—81° (*picrate*, needles, m. p. 242—244°). N-*Benzoyl*-β-*vinyldiacetonalkamine*, obtained by benzoylation of the β-alkamine base, forms leaflets, m. p. 121—122°; the O-*benzoyl* derivative, obtained by benzoylating the hydrochloride, forms needles or plates, m. p. 269—271°. Its *picrate* has m. p. 256—258°. l-iso-β-*Eucaine* d-α-*bromocamphor*-π-*sulphonate* forms needles, m. p. 236—238°, and has $[\alpha]_{5461}$ +52·1°, and $[M]_{5461}$ +290·9°, whence $[M]_{5461}$ for the *l-iso*-β-eucainium-ion is −55·6°. d-iso-β-*Eucaine* d-α-*bromocamphor*-π-*sulphonate* forms needles containing 0·5—1 mol. H_2O, the anhydrous salt having $[\alpha]_{5461}$ +70°, $[M]_{5461}$ +390°, whence the *d-iso*-β-eucainium-ion has $[\alpha]_{5461}$ +17·8°. d-iso-β-*Eucaine hydrochloride* forms needles, m. p. 271—273°, $[\alpha]_{5461}$ +14·9°. The l-*hydrochloride* has m. p. 271—273°, and $[\alpha]_{5461}$ −14·25°. The l-*picrate* forms needles, m. p. 280°. d-β-*Vinyldiacetonalkamine hydrochloride*, tablets, has m. p. 217—219°, $[\alpha]_{5461}$ +22·85°. The *base* has m. p. 121—123°; the *picrate* (needles) has m. p. 181—182°. ON-*Dibenzoyl*-α-*vinyldiacetonalkamine*, obtained by benzoylation of β-eucaine base, crystallises in plates, m. p. 142—143°. The similar *dibenzoyl* derivative from the *iso*-β-eucaine base forms prisms, m. p. 114—115°. F. G. P.

Complex Thiocyanates of Tervalent Metals. III. G. SCAGLIARINI and G. TARTARINI (*Gazzetta*, 1923, **53**, 876—878).—Unlike vanadium (A., 1923, i, 547, 1225), molybdenum forms complex thiocyanates which are highly stable and resemble, indeed, those of chromium.

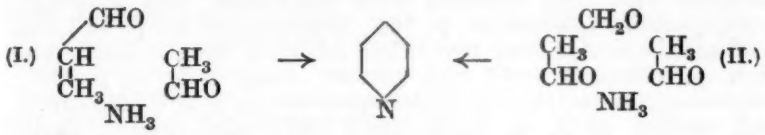
Piperidine vanadihexathiocyanate, $(C_5H_{11}N\cdot H)_3[V(SCN)_6]$, forms deep red acicular crystals; *basic pyridine vanaditetrathiocyanate*, $(C_5H_5N\cdot H)_3\left[V\begin{matrix}(SCN)_4\\(OH)_2\end{matrix}\right]$, small, brick-red crystals; *hexamethylenetetramine molybdihexathiocyanate*, $(C_6H_{12}N_4\cdot H)_3[Mo(SCN)]_6$, straw-yellow crystals; *basic pyridine molybdipentathiocyanate*, $(C_5H_5N\cdot H)_3[Mo(SCN)_5OH]$, orange-yellow crystals; and *basic piperidine molybdipentathiocyanate*, $(C_5H_{11}N\cdot H)_3[Mo(SCN)_5OH]$, brick-red crystals.

T. H. P.

Galegine. BARGER and WHITE.—(See i, 272.)

The Synthesis of Pyridine from Aldehydes and Ammonia. A. E. TSCHITSCHIBABIN and (MLLE.) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 601—606; cf. A., 1923, i, 1121 *et seq.*).—Pyridine can theoretically be formed by the interaction of ammonia either with one molecule of acraldehyde and one of acetaldehyde

(scheme I) or with two molecules of acetaldehyde and one of formaldehyde (scheme II), thus :



Either scheme would account for the formation of small quantities of pyridine in the experiments of Stöhr (A., 1891, 579; 1892, 628), because it is well known that acraldehyde is formed from formaldehyde and acetaldehyde and that the process is reversible.

It is now shown that mixtures of acraldehyde and acetaldehyde or of acetaldehyde and ethylal can be made to react with ammonia under the influence of alumina (*loc. cit.*), yielding pyridine as the main product. In the former case, some β-picoline and a small quantity of α-picoline were also obtained, whilst in the second case α-, β-, and γ-picoline and 3 : 5-dimethylpyridine were isolated in small quantities. The formation of β-picoline from ethylal, acetaldehyde, and ammonia is doubtless due to the intermediate formation of acraldehyde, which then reacts with ammonia, whilst pyridine can be produced according to either scheme (I) or (II).

G. A. R. K.

4-Methyl-2-ethylpyridine. A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 607—610).—Pure γ-picoline, regenerated from its picrate, was heated with ethyl iodide in sealed tubes at 310—325° and the new base isolated in the form of its *picrate*, short yellow prisms, m. p. 120—121°; the *base*, regenerated from this picrate, boiled at 172° and was characterised by the formation of the *chloroplatinate*, short, sparkling, orange prisms, m. p. 176° (decomp.), and the *chloroaurate*, yellow prisms, m. p. 80°. The synthesis of 4-methyl-2-ethylpyridine has since been described by Eckert and Loria (A., 1918, i, 79), but the properties of the derivatives prepared by them differ somewhat from those given above.

G. A. R. K.

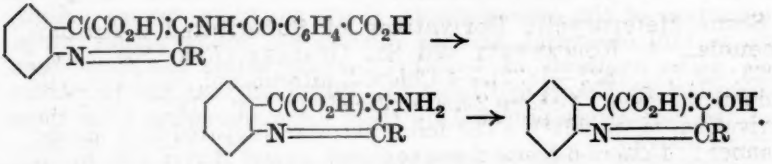
The Condensation of Acetylene with Ammonia in the Presence of Alumina. A. E. Tschitschibabin and P. A. Moschkin (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 611—624).—A preliminary account of this work has already been published (A., 1915, i, 638); a detailed description is now given of the method of synthesis and of the separation of the pyridine bases formed by the fractional precipitation of their picrates. Pyrrole bases were found to be present; of the crude condensation product, some 30% consisted of picolines, which were isolated in the form of their picrates and, by crystallising the latter from acetone, were shown to consist of the α-compound with small quantities of the γ-isomeride. The collidine fraction constituted about 10% of the original mixture. The separation was again effected through the picrates, which were crystallised from ethyl acetate. The presence

of β-collidine (4-methyl-3-ethylpyridine, chloroaurate, m. p. 140—141°, chloroplatinate, m. p. 215° [decomp.], picrate, m. p. 149°), identical with that obtained from cinchonine, and 2-methyl-5-ethylpyridine (picrate, m. p. 164°, chloroaurate, m. p. 88°) was confirmed. In addition, two other *collidines* were isolated, one of b. p. 178—182°/756·7 mm. (*picrate*, orange rods, m. p. 143°; *chloroaurate*, m. p. 119—121°; *chloroplatinate*, m. p. 207° [decomp.]), and another of b. p. 185·5—186·5°/756·7 mm. (*picrate*, short, flattened, orange needles, m. p. 134°; *chloroaurate*, plates, m. p. 116—118°; *chloroplatinate*, orange crystals, m. p. 210° [decomp.]). These collidines do not appear to be identical with 4-methyl-2-ethylpyridine (preceding abstract) or with either 2 : 3 : 4- or 2 : 3 : 6-trimethylpyridine which might possibly have been produced; but it is thought that the compounds may not be pure.

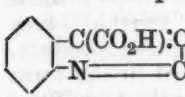
G. A. R. K.

The Absorption Spectra of some Indole Derivatives. F. W. Ward (*Biochem. J.*, 1923, **17**, 891—897).—Using the Hilger ultra-violet spectrum photometer, the absorption spectra of the following compounds have been charted: indole, indole-3-carboxylic acid, indole-3-aldehyde, indole-3-ethyl alcohol, indole-3-propionic acid, indole-3-alanine (tryptophane), 2 : 3-dihydroxyindole, 2-hydroxy-3-indole-aldehyde, isatin, and sodium indigotinsulphonate. The effect of substitution in the indole nucleus is discussed. J. P.

Certain Quinoline-4-carboxylic Acids. S. Berlingozzi and C. Marzella (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 403—406; cf. A., 1923, i, 482, 847).—The action of acetonyl- or phenacylphthalimide on isatoic acid gives rise, in the usual way, to compounds of the type:



When heated beyond their melting points, all these quinoline-4-carboxylic acids lose carbon dioxide, yielding the corresponding 3-amino- and 3-hydroxy-quinolines (*loc. cit.*). Those of the above acids which have a phenyl group in the 2-position may be regarded as derivatives of 2-phenylquinoline-4-carboxylic acid so largely used in therapeutics.



The *compound* (annexed formula) obtained from isatoic acid and acetonylphthalimide, crystallises in minute, white needles, m. p. 267—268° (decomp.).

3-Amino-2-methylquinoline-4-carboxylic acid, $C_{11}H_{10}O_2N_2$, obtained, together with phthalic acid, when the preceding compound is boiled with concentrated hydrochloric acid, forms lemon-yellow

prisms, m. p. 232—233° (decomp.), yields solutions which develop fluorescence on addition of a mineral acid, and gives 3-amino-2-methylquinoline when heated at 233—235°. Its *acetyl* derivative forms a white, microcrystalline powder, m. p. 272—273°.

3-*Hydroxy*-2-*methylquinoline*-4-*carboxylic acid*, prepared by the action of nitrous acid on the preceding amino-compound, forms minute, pale yellow crystals, m. p. 229—230° (decomp.), and is converted into 3-hydroxy-2-methylquinoline when fused; its alcoholic solutions are fluorescent and are coloured red by ferric chloride.

The *compound* formed by condensation of isatoic acid with phenacylphthalimide crystallises in lustrous, straw-yellow scales, m. p. 260° (decomp.).

3-*Amino*-2-*phenylquinoline*-4-*carboxylic acid* forms pale yellow needles and prismatic plates, m. p. 226° (decomp.), exhibits fluorescence in acid solution, and gives 3-amino-2-phenylquinoline when heated. Its *acetyl* derivative crystallises in lustrous, white scales, m. p. 257—258°.

3-*Hydroxy*-2-*phenylquinoline*-4-*carboxylic acid* is obtained as a lemon-yellow, microcrystalline powder, m. p. 206—207°, forms fluorescent alcoholic solutions which are reddened by ferric chloride, and gives 3-hydroxy-2-phenylquinoline when heated. T. H. P.

The Absorption Spectra of Kynurenic Acid and some Related Quinoline Compounds. F. W. Ward (*Biochem. J.*, 1923, **17**, 903—906).—The absorption spectra of quinoline, quinaldine, lepidine, quinaldinic acid, 2 : 6-dimethylquinoline, kynurenic acid, and of quinolylacetaldehyde have been mapped. The last-mentioned compound gives an abnormal spectrum and doubts are expressed as to its constitution. The effects of substituents in the quinoline nucleus are discussed. J. P.

Some Heterocyclic Derivatives of Substituted *o*-Aminophenols. A. Korczynski and St. Obarski (*Bull. Soc. chim.*, 1923, **33**, [iv], 1823—1832).—4-Chloro-2-nitrophenol, on electrolytic reduction, gave 4-*chloro*-2-*aminophenol* (m. p. 185°; *diacetyl* derivative, m. p. 201°). The following were prepared in a similar manner: 4-*chloro*-6-*bromo*-2-*aminophenol* (*acetyl* derivative, m. p. 150°), 4-bromo-2-aminophenol, 4 : 6-dibromo-2-aminophenol, and 4 : 6-di-iodo-2-aminophenol.

4-Chloro-2-aminophenol, on heating with acetamide (cf. Niementowski, A., 1898, i, 210) gave 4-*chloro*-1-*methylbenzoxazole* (m. p. 63°). The following compounds were obtained in a similar manner: 4-*bromo*-1-*methylbenzoxazole* (m. p. 70°), 4-*chloro*-6-*bromo*-1-*methylbenzoxazole* (m. p. 117°), and 5 : 6-*dibromo*-1-*methylbenzoxazole* (m. p. 127°). All the above oxazoles form yellow needles.

4-Chloro-2-aminophenol was converted (cf. Chetmicki, A., 1887, 477) by thiocarbonyl chloride, in presence of pyridine, into 4-*chloro*-1-*thiolbenzoxazole* (m. p. 283°), and the following compounds were prepared in a similar manner: 4-*chloro*-6-*bromo*-1-*thiolbenzoxazole* (m. p. 228°) and 4 : 6-*dibromo*-1-*thiolbenzoxazole* (m. p. 235°). All the above thiol derivatives form yellow needles, soluble in alkali.

4-Bromo-2-aminophenol (2 mols.) on boiling in alcoholic solution with chloroanil (1 mol.) affords 8-*bromo*-4-*aminophenoxazone* (giving a blue solution in concentrated sulphuric acid), the following compounds being similarly prepared: 8-*chloro*-2 : 10-*dibromo*-4-*aminophenoxazone* (reddish-violet solution in concentrated sulphuric acid), 2 : 8 : 10-*tribromo*-4-*aminophenoxazone*, and 2 : 8 : 10-*tri-iodo*-4-*aminophenoxazone* (blue solution in concentrated sulphuric acid). The above phenoxazones form red needles, not melting at 300°.

Chloroanil converts 4-nitro-2-aminophenol into a *substance* which forms orange-red needles. E. E. T.

Diphenylyl Phenylenediamines and the Colour of their Oxidation Products. J. PICCARD and F. ABOUCHY (*Helv. Chim. Acta*, 1924, **7**, 75—83).—To compare the auxochromic effect of the diphenylyl group, $Ph{\cdot}C_6H_4-$, with those of phenyl and alkyl groups, the following derivatives of *p*-phenylenediamine were prepared, for oxidation into *meri*-quinonoid salts: *s*-di-*p*-diphenylyl-*p*-phenylenediamine (I); *s*-diphenyldi-*p*-diphenylyl-*p*-phenylenediamine (II), and tetra-*p*-diphenylyl-*p*-phenylenediamine (III). To prepare the first compound, (I), *p*-dibromobenzene was condensed with *p*-acetamidodiphenyl, giving s-*diacetyldi*-p-*diphenylyl*-p-*phenylenediamine*, colourless crystals, m. p. 245°. By alkaline hydrolysis this gave s-*di*-p-*diphenylyl*-p-*phenylenediamine*, long, colourless spangles, m. p. 256°. The second base, (II), was prepared in two ways, (*a*) by condensing (I) with iodobenzene, and (*b*) by condensing *p*-iododiphenyl with *s*-diphenyl-*p*-phenylenediamine. s-*Diphenyldi*-p-*diphenylyl*-p-*phenylenediamine* forms small crystals, m. p. 211°. The third base, (III), was also obtained in two ways, (*a*) by condensing (I) with *p*-iododiphenyl, and (*b*) by condensing *p*-di-iodobenzene with di-*p*-diphenylylamine. The product, *tetra*-p-*diphenylyl*-p-*phenylenediamine*, forms small, colourless crystals, m. p. 280°. Of these three bases, only the first can be oxidised to a quinonedi-imine. By oxidation with chromic acid, it gives *di*-p-*diphenylylbenzoquinonedi-imine*,

$$Ph{\cdot}C_6H_4N{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}Ph,$$

a red, amorphous powder, m. p. 266°. It is less basic than diphenylbenzoquinonedi-imine, and the colours of its salts are deeper; its mono-acid salts are blue, di-acid salts violet, and *meri*-quinonoid salts green. meri*Di*-p-*diphenylylbenzoquinonedi-imonium picrate*,

$$[Ph{\cdot}C_6H_4NH{:}C_6H_4{:}NH{\cdot}C_6H_4{\cdot}Ph::: Ph{\cdot}C_6H_4NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4Ph][C_6H_2(NO_2)_3O]_2,$$

forms a bluish-green powder, m. p. 208°. A picrate of the *meri*-quinonoid salt of the second base was also isolated; it forms a yellowish-green powder, m. p. 169°. The colours of the *meri*-quinonoid salts of the three bases in solution are respectively bluish-green, green, and yellowish-green. The colours of the *holo*-quinonoid salts are only developed in concentrated sulphuric acid solution, and are respectively violet, bluish-violet, and blue. It is noted that glacial acetic acid dissolves the quinonedi-imine compounds as bases, the colour of the salts being developed only on addition of water. The leuco-compounds are weaker bases

than the *holo*-quinonoid compounds, but the *meri*-quinonoid compounds are stronger bases than either of these. The auxochromic effect of the diphenylyl group in *meri*-quinonoid salts in the phenylenediamine, benzidine, or fuchsine series is less than that of two phenyl groups, but considerably greater than that of one group. The phenylated salts in the benzidine series are deeper in colour than the diphenylylated salts in the phenylenediamine series. The difference between the effect of the phenyl and diphenylyl groups is more marked in the *holo*-quinonoid than in the *meri*-quinonoid salts. It may be stated as a general rule that the weight of a group has more effect in the active chromophore than in an auxochromic group. E. H. R.

The Reaction of Carbon Disulphide on *p*-Phenylenediamine. C. E. Bolser and E. B. Hartshorn (*J. Amer. Chem. Soc.*, 1923, **45**, 2349—2355).—When *p*-phenylenediamine and carbon disulphide are boiled in alcoholic solution (Pawlewski, A., 1899, ii, 405), a small quantity of *pp'*-diaminodiphenylthiocarbamide is produced, together with an insoluble compound, which has been described as *p*-phenylenethiocarbamide, $C_6H_4<^{NH}_{NH}>C{:}S$ (Lellmann, A., 1883, 185). This compound is now shown to be *di*-p-*phenylenedithiocarbamide*, $C_6H_4<^{NH\cdot CS\cdot NH}_{NH\cdot CS\cdot NH}>C_6H_4$. In the first place, its formation may be almost entirely suppressed, the yield of diaminodiphenylthiocarbamide being correspondingly increased, by conducting the process in aqueous solution, by keeping the temperature of reaction low, and by decreasing the concentration of carbon disulphide. It is advisable frequently to remove, by filtration, the diaminodiphenylthiocarbamide, which is less soluble in warm alcohol than in hot, and still less soluble in water. This suggests that the simple thiocarbamide is an intermediate stage in the formation of the insoluble compound; that this is actually so is shown by the formation of the latter when carbon disulphide and *pp'*-diaminodiphenylthiocarbamide react in boiling alcoholic solution. The identity of the product with that formed directly from carbon disulphide and *p*-phenylenediamine is shown (although in neither reaction is an absolutely pure substance obtained) by the temperature of decomposition (285°), by the formation of *p*-phenylenediamine by the action of hot, concentrated acids, and by the formation of *p*-phenylenedithiocarbimide by the prolonged action of boiling acetic anhydride. The latter reaction proves that the compound has the above structure, since *p*-phenylenethiocarbamide could not give the dithiocarbimide, but should be converted into p-*acetamidophenylthiocarbimide*, white needles, m. p. 195—196°. The latter is produced by the action of boiling acetic anhydride on *di*-p-*acetamidophenylthiocarbamide*, a white solid, m. p. 235—237°, which is formed by the action of an excess of carbon disulphide on *p*-aminoacetanilide in boiling alcoholic solution. It was hoped that the hydrolysis of this derivative, which requires the use of hot, concentrated hydrochloric acid,

might give di-*p*-aminophenylthiocarbamide (thus avoiding the concurrent formation of the insoluble compound), but actually phenylenediamine hydrochloride is the sole product.

The reduction, by means of stannous chloride and a mixture of glacial acetic acid and concentrated hydrochloric acid, of *azobenzene*-p-*thiocarbimide*, $Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NCS$, salmon-coloured needles, m. p. 94—95°, which is obtained by heating thiocarbonyl chloride and *p*-aminoazobenzene in carbon tetrachloride solution at 100°, gives diphenylenedithiocarbamide, but the latter does not appear until the solution is made alkaline. It is probable that the acid solution contains, in equilibrium with the dimeric compound, *p*-aminophenylthiocarbimide (hydrochloride). In fact, when the acetyl derivative (above) of the latter compound is boiled with glacial acetic acid, in the presence of this weaker acid diphenylenedithiocarbamide is precipitated, more of the same material being thrown down on dilution. It is evident that the tendency to the formation, by what is practically a tautomeric change, of this substance is so great, that free *p*-aminophenylthiocarbimide cannot exist, but, on liberation from its salts, immediately undergoes polymerisation. W. S. N.

New Methods of Splitting Pyrimidines. III. The Action of Iodine Solution on Pyrimidines. L. W. Bass and O. Baudisch (*J. Amer. Chem. Soc.*, 1924, **46**, 181—183; cf. A., 1922, ii, 328).—Pyrimidines with unsubstituted nitrogen atoms and with a double bond between carbon atoms 4 and 5 absorb iodine from solution in the presence of sodium bicarbonate. On distillation of the reaction mixtures, after removal of excess iodine, carbamide is found in the residues as a scission product. No carbamide can be detected before the distillation. Substitution by an alkyl group in position 5 retards the rapidity of decolorisation of iodine solution. Hydrouracil decolorises iodine solution, but no carbamide is formed when the reaction mixture is distilled. 1 : 3-Dimethylthymine does not decolorise iodine solution. Thymine itself yields carbamide and acetol; no pyruvic acid is formed. When bromine is substituted for iodine, the pyrimidine ring is not split under the conditions of the experiments. F. A. M.

New Methods of Splitting Pyrimidines. IV. A Study of the Mechanism of the Decomposition of Thymine. O. Baudisch and L. W. Bass (*J. Amer. Chem. Soc.*, 1924, **46**, 184—189; cf. preceding abstract).—The action of various oxidising agents on thymine has been studied; the primary products of the reactions still contain the carbamide residue. The final products, carbamide, acetol, and pyruvic acid, are formed only when the primary products are heated in aqueous solution with sodium hydrogen carbonate. Acetol is formed as a direct hydrolytic product of thymine, whilst pyruvic acid is formed by the complete hydrolysis of an intermediate oxidation product. A mechanism is suggested to explain the decomposition of thymine under the conditions used. F. A. M.

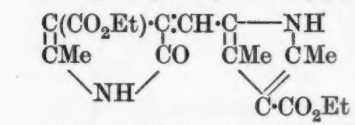
New Methods of Splitting Pyrimidines. V. The Action of Oxygen plus Ferrous Salts on Thymine under the Influence of Light. L. W. Bass (*J. Amer. Chem. Soc.*, 1924, **46**, 190—192; cf. preceding abstracts).—When in an atmosphere of oxygen aqueous solutions of thymine are illuminated using a quartz mercury arc, the pyrimidine is split to some extent into carbamide and pyruvic acid; no acetol is formed. The reaction is accelerated, but otherwise not affected, by ferrous sulphate or, to a smaller extent, by potassium ferrocyanide. No scission occurs in an atmosphere of nitrogen even in the presence of the above salts. F. A. M.

Catalysis. III. Reduction of Uracil to Hydrouracil. E. B. Brown and T. B. Johnson (*J. Amer. Chem. Soc.*, 1923, **45**, 2702—2708; cf. A., 1921, i, 806; 1922, i, 709).—Further experimental details are given, relating to the reduction of uracil to hydrouracil by means of hydrogen, in the presence of colloidal platinum. Colloidal palladium may also be used. Sulphur compounds, even when present only as traces, completely inhibit the reaction, but the chlorides of sodium, potassium, calcium, and magnesium are quite without effect. W. S. N.

Synthetic Researches on the Constitution of Bile-pigments. II. H. Fischer and J. Müller (*Z. physiol. Chem.*, 1924, **132**, 73—103).—If dry ammonia is passed through a cold alcoholic solution of ethyl α-acetyl-β-methylsuccinate, crystals are obtained, m. p. 77° (decomp.), apparently of ethyl β-amino-Δ^{β}-pentene-γδ-dicarboxylate, which on keeping or on warming in a vacuum at 40—50° completely change into ethyl 2-hydroxy-3 : 5-dimethylpyrrole-4-carboxylate, m. p. 127°, a compound which is also found in the mother-liquors from the crystals. This pyrrole derivative, when warmed in 50% sulphuric acid, yields α-methyl-lævulic acid, and when treated with hydrazine hydrate, is converted into the *hydrazide* of 2-hydroxy-3 : 5-dimethylpyrrole-4-carboxylic acid, sharp-angled leaflets, decomposing at 212°. This compound may be converted by nitrous acid into the *azide* of 3 : 5-dimethyl-2-hydroxypyrrole-4-carboxylic acid, flat prisms, which decompose explosively at 114°, and this compound, in solution in boiling absolute ethyl alcohol, yields *ethyl 2-hydroxy-3 : 5-dimethylpyrryl-4-carbamate*, white needles, decomposing at 148°, whilst if methyl alcohol is used, the corresponding *methyl carbamate* is obtained as white, glistening needles, decomposing at 164°. From ethyl acetylsuccinate, the following corresponding series of compounds is obtained: *ethyl β-amino-Δ^{β}-butene-γδ-dicarboxylate*, m. p. 122—124° (decomp.); ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate, m. p. 134°; (*hydrazide*, leaflets, decomposing at 232°; *azide*, needles, which decompose explosively at 135°; *methyl carbamate*, needles, m. p. 175°).

Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate condenses with aldehydes in alcoholic solution in presence of hydrochloric acid, and the following compounds are described: *ethyl 2-keto-3-benzylidene-5-methyl-2 : 3-dihydropyrrole-4-carboxylate*, yellow leaflets,

m. p. 184°; *ethyl* 2-*keto*-3-p-*dimethylaminobenzylidene*-5-*methyl*-2 : 3-*dihydropyrrole*-4-*carboxylate*, red needles from alcohol, m. p. 231° (*hydrochloride*, yellow needles, unstable in air, decomposing at 210°, *perchlorate*, yellow needles, stable in air, m. p. 150° [decomp.]); *ethyl* 2-*keto*-3-o-*nitrobenzylidene*-5-*methyl*-2 : 3-*dihydropyrrole*-4-*carboxylate*, felted yellow needles, m. p. 201°; 4-*carbethoxy*-2-*hydroxy*-5-*methylpyrrolidyl*-3′-*carbethoxy*-2′ : 4′-*dimethylpyrrylmethene* (annexed formula), orange-yellow prisms, m. p. 210°, with which is also formed a *compound* (deep orange-yellow prisms, m. p. 162—163°); and 4-*carbethoxy*-2-*hydroxy*-5-*methylpyrrolidyl*-5′-*carbethoxy*-2′ : 4′-*dimethylpyrrylmethene*, needles, m. p. 266°.

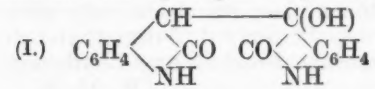
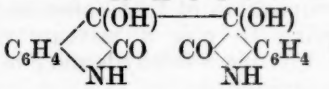


Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate couples with benzene-diazonium chloride to give a *dye*, $C_{14}H_{15}O_3N_3$ (glistening, pure yellow, felted needles, m. p. 233°), which forms a *sodium* salt, $C_{14}H_{14}O_3N_3Na$, red needles, and a *potassium* salt, orange-yellow needles. When treated with ammoniacal copper solution the dye is converted into an isomeric *compound* (large orange-red to dark red, transparent needles, decomposing at 213°), which on crystallisation from alcohol yields the original dye. The latter, when reduced with zinc dust in hot alcoholic solution or with hydrogen in presence of platinum black, yields ethyl 3-amino-2-hydroxy-5-methylpyrrole-4-carboxylate, m. p. 244° (cf. Fischer and Herrmann, A., 1922, i, 1054). *Dyes* obtained similarly from *m*-nitrobenzene-diazonium chloride and from α-naphthalene-diazonium chloride, form thin, yellow, bunched needles, m. p. 233°, and red needles, decomposing at 234°, respectively. The application of the Gattermann reaction to ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate yields, besides a *by-product* which decomposes at 262°, the *aldimine*, $C_9H_{12}O_3N_2$, colourless leaflets, m. p. 241°, which is not hydrolysed by water to the aldehyde, and is decomposed by alkalis with the liberation of ammonia. The *aldehyde*, however, may be obtained when sodium is added to a boiling mixture of ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate and ethyl formate, and forms large, flat needles, m. p. 206°. It yields a *semicarbazone*, bunched needles, m. p. 252° (with previous browning and sintering), and a *hydrazone*, small rods, m. p. 190°. It condenses with ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate to yield 4-*carbethoxy*-3-*hydroxy*-5-*methylpyrrolidyl*-4′-*carbethoxy*-2′-*hydroxy*-5′-*methylpyrrylmethene*, yellow needles, m. p. 250°, and with ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate to yield bis-(4-*carbethoxy*-2-*hydroxy*-5-*methylpyrryl*)*methene*, brownish-yellow prisms, m. p. 254°. 4-*Carbethoxy*-3-*hydroxy*-5-*methylpyrrole*-2-*aldehyde*, faintly coloured needles, m. p. 188°, is obtained when ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate is condensed with ethyl formate in presence of sodium. Ethyl oxalate, similarly, condenses with ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate to form *ethyl* 4-*carbethoxy*-2-*hydroxy*-5-*methylpyrryl*-3-*glyoxylate*, glistening prisms, m. p. 180°, and with ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate to yield *ethyl* 5-*carbethoxy*-2 : 4-*dimethyl*-

pyrryl-3-ethanonoxalate, fine, colourless, felted needles, m. p. 150·5°. The latter is readily decomposed by alkalis to yield 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate, and forms a *semicarbazone*, m. p. 201°, and a *ketazine-hydrazide*, $C_{13}H_{17}O_3N_5$, needles, m. p. 239° (decomp.). Ethyl 2 : 4-dimethylpyrryl-3-ethanonoxalate forms a *semicarbazone*, m. p. 198° (decomp.). Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, when heated with hydrazine hydrate at 200° in a closed tube, yields 2 : 4-dimethylpyrrole. If 1′-*p*-toluoyl-4-carbethoxy-3-hydroxy-5-methylpyrrolidyl-3′-carbethoxy-2′ : 5′-dimethylpyrrylmethene is treated with benzene-diazonium chloride, decomposition of that compound takes place simultaneously with coupling to give a mixture of 3-carbethoxy-2 : 5-dimethyl-1-*p*-toluylpyrrole-4-aldehyde and 2-benzeneazo-4-carbethoxy-3-hydroxy-5-methylpyrrole. W. O. K.

Oxidation–Reduction. IV. Electrode Potentials of Indigotinsulphonates. M. X. Sullivan, B. Cohen, and W. M. Clark (*U.S. Public Health Repts.*, 1923, **38**, 1669—1718).—A survey of the literature shows conflicting statements regarding the behaviour of indigotin and its sulphonates in vitro and in vivo, and a lack of satisfactory theories due to lack of quantitative data for the oxidation–reduction equilibrium. Indigotin-mono-, -di-, -tri-, and -tetra-sulphonates were prepared by Bloxam's method (A., 1906, ii, 819), and the electrode potentials at 30° were determined by elaboration of methods already described (A., 1923, ii, 726, etc.). The experimental results were in accord with the rational equation : $E_h = E_o - [(RT/nF) \log_e (S_r/S_o)] + (RT/nF) \log_e [K_1(H^+) + (H^+)^2]$, where E_h is the observed electrode potential referred to the hydrogen standard, S_r and S_o are the concentrations of total reductant and total oxidant, (H^+) is the hydrogen-ion concentration of the solution, and K_1 the acid dissociation constant of one of the two hydrogen atoms of the hydrogenated leuco-compound (dissociation of the sulphonic acids not being considered). The number, n, of electrons in the reversible oxidation–reduction is 2. The second acidic hydrogen atom of the leuco-compound has a dissociation constant below 10^{-12}. The values of E_o and K_1 were as follows : indigotinmonosulphonate $\rightleftharpoons$ leuco-compound, +0·262, $1·6 \times 10^{-8}$; indigotindisulphonate $\rightleftharpoons$ leuco-compound, +0·291, $4·9 \times 10^{-8}$; indigotintrisulphonate $\rightleftharpoons$ leuco-compound, +0·332, $7·7 \times 10^{-8}$; indigotintetrasulphonate $\rightleftharpoons$ leuco-compound, +0·365, $11·2 \times 10^{-8}$. Indigotin $\rightleftharpoons$ indigo-white is not adapted to accurate experiments in aqueous solution. Approximate data indicate $K_1 = 10^{-8}$ and E_o near that of the monosulphonate. Anomalies with borate buffers are shown, and evidence is given of a " salt effect " with other buffer systems, of the acidic nature of the leuco-compounds, and of the ionisation of only one hydrogen atom at moderate alkalinities. An electrometric method of analysis of mixtures of the sulphonates is developed. The data cover all conditions for the reversible oxidation–reduction of an indigotinsulphonate and give their properties for use in colorimetric determinations of oxidation–reduction intensities of biological solutions. Chemical Abstracts.

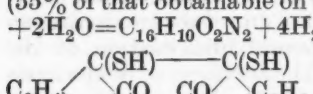
Constitution of Isatan and Isatide. A. WAHL and W. HANSEN (*Compt. rend.*, 1924, **178**, 393—396; cf. following abstract).—Isatan (I), $C_{16}H_{12}O_3N_2$, on heating in boiling naphthalene solution, affords indine (cf. Laurent, *Ann. Chim. Phys.*, 1840, [iii], **3**, 469); it results from the condensation of oxindole and isatin in presence of piperidine (cf. Stollé, A., 1914, i, 992), and is the product called isatide by Erdmann (*J. pr. Chem.*, 1840, [i], **24**, 1), who treated isatin with excess of ammonium hydrosulphide. Isatan was obtained by Laurent (*loc. cit.*) by reducing disulphoisatide with ammonium hydrogen sulphite. Isatide, $C_{16}H_{12}O_4N_2$ (II), which

(I.)  (II.) 

does not give indine on heating, is the product obtained by Laurent by treating isatin with a slight excess of ammonium hydrosulphide, and by Heller (A., 1904, i, 416) by reducing isatin with zinc and acetic acid. Isatide is formed rapidly when a mixture of dioxindole and isatin is treated, in alcoholic solution, with piperidine.

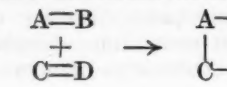
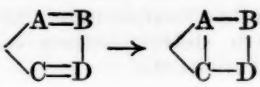
E. E. T.

Transformation and Constitution of Disulphoisatide. A. WAHL and W. HANSEN (*Compt. rend.*, 1924, **178**, 214—216).—The formula, $C_{16}H_{12}O_2N_2S_2$, given by Laurent (*Ann. Chim. Phys.*, 1840, [iii], **3**, 469) to disulphoisatide has been confirmed. The formation of indine by the action of alkali on disulphoisatide is shown to depend on the nature and concentration of the alkali used, and not to occur if air is excluded. The conversion is best effected by adding aqueous sodium carbonate to an aqueous-alcoholic solution of disulphoisatide. Isatin is produced simultaneously (55% of that obtainable on the basis of the equation : $2C_{16}H_{12}O_2N_2S_2 + 2H_2O = C_{16}H_{10}O_2N_2 + 4H_2S + 2C_8H_5O_2N$). Sulphur is initially formed, and reduces indine to leuco*iso*-indigotin, which is oxidised if air is present. The annexed formula (cf. Kohn and Ostersetzer, A., 1916, i, 607, and Lefèvre, *ibid.*, 430) is proposed for disulphoisatide, a disulphide formula being excluded, since on reduction it gives leuco*iso*-indigotin (A., 1923, i, 607).



E. E. T.

The Additive Formation of Four-membered Rings. III. The Nomenclature of Four-membered Rings and the Formation and Properties of some Derivatives of Methylene-1 : 2 : 4-oxadi-imine. C. K. INGOLD (*J. Chem. Soc.*, 1924, **125**, 87—102).—It has been found that the formation of a four-membered ring, by the additive union of double bonds (I) is of considerable generality, and this confirms the prediction (T., 1922, **121**, 2793) made from the analogy with the tautomeric change or internal addition reaction shown in (II) :

(I.)   (II.)

A system of nomenclature is proposed for the new heterocyclic ring types that have been already produced. Part of the object of the work is to discover which of these types are the most stable. It has been shown earlier (*loc. cit.*, and T., 1923, **123**, 2745) that certain types of azomethines and nitroso-compounds pass into stable cyclic bimerides. It is now shown that an azomethine and a nitroso compound of the particular type combine additively to give a stable 1 : 2 : 4-oxadi-imine (annexed formula). *Methylene*-p-*chloroaniline*, $CH_2{:}N{\cdot}C_6H_4Cl$, forms needles, m. p. 142°, the corresponding p-*bromo*-derivative, needles, having m. p. 169°. p-*Chloronitrosobenzene* has m. p. 90°, the corresponding *bromo*-derivative having m. p. 94°. The following compounds are also described: 2-*phenyl*-4-p-*tolylmethylene*-1 : 2 : 4-*oxadi-imine* (needles, m. p. 150°); the similar 4-p-*chlorophenylmethylene* compound (needles, m. p. 162°); the 4-p-*bromophenyl* compound (needles, m. p. 171°); 4-p-*chlorophenyl*-2-p-*tolylmethylene-oxadi-imine* (needles, m. p. 163°); the 4-p-*bromophenyl* derivative (m. p. 158°), the 2 : 4-*dichloro*-derivative (m. p. 171°), and the 2 : 4-*dibromo*-derivative (m. p. 175°). p-*Chlorophenylcarbylamine* forms needles (m. p. 71°), the corresponding *bromocarbylamine* having m. p. 99°. Both have an odour somewhat less powerful than that of phenylcarbylamine itself, but the taste of the vapour is considerably stronger. 2-p-*Chlorophenyl*-4-p-*bromophenylmethylene*-1 : 2 : 4-*oxadi-imine* forms needles, m. p. 171°.

Phenyl-p-*tolylcarbodi-imide*, $C_6H_4Me{\cdot}N{:}C{:}NPh$ (b. p. 170/12° mm.) (converted by aqueous-alcoholic hydrochloric acid into phenyl-*p*-tolylcarbamide), *phenyl*-p-*chlorophenylcarbodi-imide* (b. p. 175/11° mm.), p-*bromodiphenylcarbodi-imide* (b. p. 185/11° mm.), p-*chlorophenyl*-p-*tolylcarbodi-imide* (b. p. 175°/10 mm.), p-*bromophenyl*-p-*tolylcarbodi-imide* (b. p. 188°/10 mm.), pp′-*dichlorodiphenylcarbodi-imide* (b. p. 190°/10 mm.), pp′-*dibromodiphenylcarbodi-imide* (b. p. 202°/10 mm.), and p-*chloro*-p′-*bromodiphenylcarbodi-imide* (b. p. 198—200°/11 mm.) are, like the phenyl-*p*-tolyl derivative, viscous liquids, their constitutions being proved by conversion into the corresponding carbamides.

p-*Chlorophenyl*-p-*tolylcarbamide* (needles, m. p. 297—299° [decomp.]), p-*bromophenyl*-p-*tolylcarbamide* (needles, m. p. 316—318° [decomp.]), and p-*chloro*-p′-*bromodiphenylcarbamide* (needles, m. p. about 300° [decomp.]) were obtained (see *ante*) from the corresponding carbodi-imides. F. G. P.

The Additive Formation of Four-membered Rings. IV. The Influence of Temperature on the Tendency towards Self-addition of the Nitroso-group. C. K. Ingold and H. A. Piggott (*J. Chem. Soc.*, 1924, **125**, 168—176).—Owing to the chromophoric character of the nitroso-group, the use of the colorimeter enables the reversible reaction 2 $N{:}O \rightleftharpoons$ to be followed in greater detail than is the case with the reactions previously studied (see preceding abstract). The influence of temperature on the equilibrium is determined for the case of nitroso-

mesitylene in benzene solution. Using these results, the order of the reaction is calculated from certain equations, and shown to be in accordance with the chemical evidence. Nitrosomesitylene, the preparation of which (and of mesidine) from dimethylaniline is described, has m. p. 122—123° (cf. Pechmann and Nold, A., 1898, i, 310). The heat absorbed during the dissociation of 1 g.-mol. of dimeric nitrosomesitylene is calculated to be about 13,700 g.-cal. In 3% solution in benzene, dissociation occurs to the extent of about 18%; in a 2% solution, 21·6%. This corresponds with a molecular weight 245, agreeing fairly well with Bamberger's value 246 obtained (A., 1901, i, 141) cryoscopically in benzene solution. F. G. P.

Dioximes. XVII. G. Ponzio and B. Zanardi-Lamberti (*Gazzetta*, 1923, **53**, 818—824).—In some of their properties, 5-hydroxy-3-aryl-1 : 2 : 4-oxadiazoles (or hydroxyazoximes),

$$O<\begin{matrix}N=\!=\!=C\cdot Ar\\ C(OH):N\end{matrix} \rightarrow O<\begin{matrix}N=C\cdot Ar\\ CO\cdot NH\end{matrix},$$

which are formed by withdrawal of two atoms of hydrogen from the α-modifications of monoarylglyoximes, differ considerably from the 3 : 5-diaryl-1 : 2 : 4-oxadiazoles (or azoximes), which result on elimination of a molecule of water from a *s*-diarylglyoxime. Thus, the azoximes are either completely destroyed or slowly converted into nitriles by the action of reducing agents, whereas the hydroxyazoximes are very easily reduced to amidines, $NH_2\cdot CR{:}NH$, by means of hydriodic acid in presence of red phosphorus. Further, the hydroxyazoximes exhibit acid properties, the mean values of the ionisation constant at 25° being $0{\cdot}879\times10^{-5}$, $0{\cdot}022\times10^{-5}$, and $0{\cdot}140\times10^{-5}$ for 5-hydroxy-3-phenyl-, *p*-tolyl-, and benzyl-1 : 2 : 4-oxadiazoles; thus, the *p*-tolyl compound is slightly weaker than carbonic acid, and the other two compounds are stronger.

Benzenylamidine, obtained by reduction of 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole, gives a picrate, m. p. 235°; Dieckmann (A., 1892, 705) gave m. p. 228°. According to Pinner ("Die Imidoaether," 167), 2 : 4 : 6-triphenyl-1 : 3 : 5-triazine is formed when benzenylamidine hydrochloride is heated for six hours at 120—140° with benzoyl chloride. This reaction occurs at the ordinary temperature when benzenylamidine carbonate is treated with 20% sodium hydroxide solution and benzoyl chloride.

5-Hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole, prepared from *p*-tolenylamidoxime and ethyl chlorocarbonate (cf. Schubart, A., 1890, 47), is the product of the isomerisation of the oxide of *p*-tolyl cyanide oxime (cf. Avogadro, this vol., i, 294). By hydriodic acid and red phosphorus it is converted into *p*-tolenylamidine, which forms a *picrate*, $C_6H_4Me\cdot C(:NH)\cdot NH_2,C_6H_3O_7N_3$, crystallising in yellow needles, m. p. 224—225° (decomp.), and a *carbonate*, crystallising in white laminæ, m. p. 127—128° (gas); the corresponding nitrate was described by Pinner (*loc. cit.*, 184). 5-Hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole forms the following derivatives: *sodium* salt, white powder; *silver* salt, white crystals, stable towards light; *methyl* ether, slender, white needles.

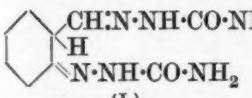
5-Hydroxy-3-benzyl-1 : 2 : 4-oxadiazole, $O<\begin{matrix}N=\!=\!=C\cdot CH_2Ph\\ C(OH):N\end{matrix}$, prepared by the action of sodium hydroxide on the ethyl phenylethenylamidoximecarboxylate obtained by the interaction of ethyl chlorocarbonate and phenylethenylamidoxime, $CH_2Ph\cdot C(:NOH)\cdot NH_2$, crystallises in large, lustrous laminæ, m. p. 115°. By hydriodic acid and red phosphorus it is converted into phenylethenylamidine, $CH_2Ph\cdot C(:NH)\cdot NH_2$, the *picrate* of which forms yellow needles, m. p. 224° (decomp.). 5-Hydroxy-3-benzyl-1 : 2 : 4-oxadiazole forms a *sodium* salt, white powder; an insoluble *silver* salt, white, crystalline powder, stable towards light, and a *methyl ether*, crystallising in needles, m. p. 112—113°.

5-Hydroxy-3-α-naphthenyl-1 : 2 : 4-oxadiazole has m. p. 196°, and not 189° as stated by Richter (A., 1890, 62). *α-Naphthenylamidine*, $C_{10}H_7\cdot C(:NH)\cdot NH_2$, crystallises in white laminæ, m. p. 154°, and its *picrate* in yellow needles, m. p. 223° (decomp.).

5-Hydroxy-3-β-naphthenyl-1 : 2 : 4-oxadiazole, m. p. 219—220° (Richter, *loc. cit.*, gave 216°), yields on reduction β-naphthenylamidine, the *picrate* of which forms reddish-yellow needles, m. p. 240° (decomp.). T. H. P.

Tetrahydroindazoles. K. von Auwers, W. Buschmann, and R. Heidenreich (*Annalen*, 1924, **435**, 277—321).—A study of the tetrahydroindazoles obtained by condensing hydrazine derivatives with hydroxymethylene*cyclo*hexanone and 1-methyl-3-hydroxymethylene*cyclo*hexan-2-one. In the preparation of the latter compound (cf. A., 1915, i, 818), acetone sodium (Freer, A., 1894, i, 65) and 1-methyl*cyclo*hexan-2-ol are formed as by-products. 1-*Methyl*-3-*benzoxymethylene*cyclo*hexan-2-one* (needles, m. p. 84—85°) is hydrolysed more readily by acids than by alkalis.

Semicarbazide reacts with hydroxymethylene*cyclo*hexanone to give tetrahydroindazole-2-carbonamide (Wallach and Steindorff, A., 1904, i, 104), the constitution of which is now definitely established by its formation by the hydrolysis of the *semicarbazone* of benzoxymethylene*cyclo*hexanone (needles, m. p. 193° if bath previously heated at 190°). Excess of semicarbazide converts the hydroxymethylene ketone into the *disemicarbazone* (I), which in hot dilute sulphuric acid solution affords the above carbonamide. The latter, as shown by Wallach (*loc. cit.*) occurs in two forms, although the latter author's m. p. observations are incorrect. The carbonamide, if obtained in the labile form (as in the first method given above), has m. p. 158°, but unless the m. p. bath is previously heated to within a few degrees of this temperature, the labile form passes, before its m. p. is reached, into the stable form (m. p. 186—188°) (see *infra*). Wallach's second m. p. (220°) actually indicated the decomposition of the carbonamide to give cyanuric acid.

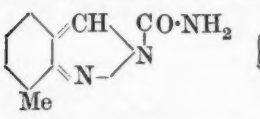


(I.)

The above disemicarbazone (I) had m. p. 193° when first prepared, but after six months, m. p. 203°. The lower m. p. is that of the labile form, which was not subsequently obtained. The substance

becomes solid after melting at 203°, re-melting, with decomposition, at 234—236°.

Methyl-hydroxymethylene*cyclo*hexanone affords (with semicarbazide in cold acetic acid solution) the normal *semicarbazone* (white needles, m. p. 193° or 203°, according to the rate of heating), the *benzoyl* derivative of the latter being identical with the *semicarbazone* (m. p. 186°) of methyl-benzoxymethylene*cyclo*hexanone. Excess of semicarbazide converts the methyl hydroxymethylene ketone into the *disemicarbazone* (prisms, m. p. 215° if heated suddenly, and 237° [decomp.]), together with a little *7-methyltetrahydroindazole-2-carbonamide*, the latter also being formed in small quantities in the preparation of the monosemicarbazone. The carbonamide exists in two forms: *labile* form, monoclinic needles, m. p. 138° (if plunged suddenly into bath just below 138°), then solidifying to give the *stable* form, tetragonal crystals, m. p. 163°. The labile form can be kept at the ordinary temperature, but passes into the stable form on heating in a toluene vapour-bath, or on boiling in alcoholic solution. The labile form results when the semicarbazone is treated in cold acetic acid solution with a little sulphuric acid, with subsequent addition of water, whereas if the solution is heated before addition of water, the latter precipitates the stable form. Again, when the parent ketone is treated with semicarbazide in presence of mineral acid, the carbonamide is formed, the production of the labile or of the stable form depending on the hydrogen-ion concentration. The carbonamide is converted by ammoniacal silver nitrate solution into the *silver* salt of 7-methyltetrahydroindazole, this salt, with carbamyl chloride, affording a mixture of the two forms of the carbonamide. The latter are shown to be



stereoisomerides (see annexed formulæ), and not structural isomerides. They are readily interconvertible; moreover, under conditions when a 1-derivative might be expected to result (as when the parent ketone is treated with semicarbazide hydrochloride), the labile form, already proved to be a 2-derivative, is obtained. Polymorphism is also excluded as an explanation of the isomerism, on experimental grounds.

Tetrahydroindazole (m. p. 84°), first obtained by Wallach (*loc. cit.*), is prepared by boiling tetrahydroindazole-2-carbonamide (or the parent semicarbazones) with mineral acids, and gives the following derivatives: *picrate*, m. p. 155—156°; *silver* salt; 2-*acetyl* derivative, b. p. 130°/15 mm.; and 2-o-*nitrobenzoyl* derivative, white needles, m. p. 129—130°.

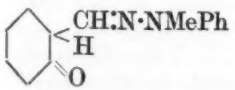
7-*Methyltetrahydroindazole* is a viscous oil, b. p. 152·8°/12 mm., becoming solid at the temperature of mixtures of ether and solid carbon dioxide. The following derivatives are described: *hydrochloride*, white prisms; *picrate*, m. p. 151—152°; *mercuric chloride additive* compound, white needles; *silver nitrate additive* compound, $Ag(C_8H_{12}N_2)_2NO_3$, white needles, m. p. 132°; *silver* salt, $C_8H_{11}N_2Ag$ (two forms, one soluble and one insoluble in ether); 2-*phenyl*-

carbonamide, white prisms, m. p. 70° (from the indazole and phenylcarbimide); and 2-o-*nitrobenzoyl* derivative, leaflets, m.p. 104—107°. The parent indazole is obtained either by treating methyl-hydroxymethylene*cyclo*hexanone semicarbazone with hot dilute sulphuric acid, or the ketone itself with hydrazine.

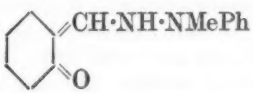
Hydroxymethylene*cyclo*hexanone, when treated with phenylhydrazine, gives a mixture of 1- and 2-phenyltetrahydroindazoles, which are not interconvertible and are separable as the picrates. The constitution of the 2-phenyl derivative follows from its formation from the benzoylated ketone and phenylhydrazine. The intermediately formed *phenylhydrazone* of the benzoylated ketone has only a transitory existence (white needles, m. p. about 80°), and rapidly passes into the above 2-phenylindazole derivative. 1-*Phenyl*-4 : 5 : 6 : 7-*tetrahydroindazole* forms leaflets, m. p. 58—59°, b. p. 178°/10 mm. (*picrate*, m. p. 125—126°, and *perchlorate* are described). 2-*Phenyltetrahydroindazole* forms prisms, m. p. 48·5—49·5°, b. p. 177°/10 mm. (*picrate*, m. p. 126·5—127·5°, and *perchlorate* are described).

In the interaction of hydroxymethylene*cyclo*hexanone and phenylhydrazine, the higher the concentration of hydrion, the smaller the proportion of 2-phenyl derivative formed, particularly if, at the same time, the temperature is kept low. Thus, when the ketone is treated at 0° with phenylhydrazine hydrochloride, only the 1-phenyl derivative is formed. This is explained as being due to the driving back, by hydrion, of the dissociation of the hydroxymethylene group, with resulting increase in the proportion of the aldehydic form, from which the 1-compound would be formed (cf. Claisen, A., 1895, i, 62). In this connexion, the nature of the hydrazine derivative affects the proportion of 1- to 2-derivative obtained, this being, under comparable conditions, as follows: phenylhydrazine, 1 : 0, *as*-phenylmethylhydrazine, 2 : 1, benzylhydrazine, 3 : 4, methylhydrazine, 4 : 1, and semicarbazide, 0 : 1.

In order to throw light on the constitution of the intermediate compounds formed in the interaction of phenylhydrazine and hydroxymethylene*cyclo*hexanone, the interaction of the latter with phenylmethylhydrazine has been studied. The main product (m. p. 170—171°) is insoluble in alkali and may be either the *phenylmethylhydrazone* of 2-*keto*cyclo*hexylformaldehyde* (II) or 1-*methylphenylhydrazidomethene*cyclo*hexan*-2-*one* (III). A second product, soluble in alkali, is the *hydrate* (needles, m. p. 123—124°) of the *acid* produced by the spontaneous oxidation of IV. There is also formed a third product (under slightly different conditions), viz., the *hydrate* of the *phenylmethylhydrazone* of 1-*formyl*cyclo*hexan*-2-*one* (needles, m. p. 125—126°).



(II.)



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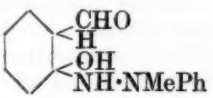


(IV.)

Methyl-hydroxymethylene*cyclo*hexanone, with phenylhydrazine, affords a mixture of the 1- and 2-indazole derivatives, low temperatures and high concentrations favouring the production of the 1-derivative. The latter is a stronger base than the 2-derivative, and forms a stable *perchlorate* (m. p. 214—215°), which allows of its separation from its isomeride. The benzoyl derivative of the methyl*cyclo*hexanone affords a *phenylhydrazone* (m. p. 125°, with previous sintering), which rapidly passes, in solution, into 2-*phenyl*-7-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazole* (a colourless oil, b. p. 181·4°/10 mm. The *methiodide*, m. p. 172°, gives 2-phenyltetrahydroindazole when heated). 1-*Phenyl*-7-*methyltetrahydroindazole* is a colourless oil, b. p. 175°/10 mm.; its *methiodide*, m. p. 154°, on heating, gives 1-phenyltetrahydroindazole.

The products of the alkylation of tetrahydroindazole depend on the nature of the alkyl group introduced and on the experimental conditions. Tetrahydroindazole, when heated in alcoholic solution with benzyl chloride in presence of alkali, or when heated alone with the chloride at water-bath temperatures, affords a mixture of the 1- and 2-benzyl derivatives, this mixture also being obtained by condensing benzylhydrazine with hydroxymethylene*cyclo*hexanone. The benzoyl derivative of the latter ketone is converted by benzylhydrazine into 2-*benzylindazole* (colourless oil, b. p. 177°/10 mm.). 1-*Benzyltetrahydroindazole* is a colourless oil, b. p. 172°/10 mm. (*picrate*, m. p. 128—129°, and *perchlorate* are described).

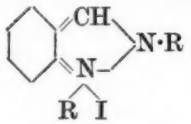
Tetrahydroindazole, when heated at 100° with ethyl bromide, gives 2-*ethyltetrahydroindazole* (a colourless oil, b. p. 118°/15 mm.; *picrate* has m. p. 150·5—151·5°), whilst when similarly heated in presence of alkali, it affords 1-*ethyltetrahydroindazole* (a colourless oil, b. p. 111°/14 mm.; *picrate* has m. p. 103—104°).

The methylation of tetrahydroindazole leads, in presence or in absence of alkali, to the formation of the 1- and 2-methyl derivatives, which cannot be separated. 2-*Methyltetrahydroindazole*, obtained from benzoxymethylene*cyclo*hexanone, is a colourless oil, b. p. 93—94°/9 mm. or 103°/13 mm. (*picrate*, m. p. 166·5—167·5°).

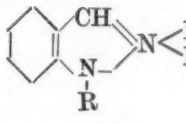
7-Methyltetrahydroindazole on methylation, ethylation, or benzylation, in presence or in absence of alkali, always affords 2-derivatives, which may be obtained from the appropriate hydrazine and methylbenzoxymethylene*cyclo*hexanone. 2 : 7-*Dimethyl*-4 : 5 : 6 : 7-*tetrahydroindazole* is a colourless oil with a feeble blue fluorescence, has b. p. 111°/13 mm., and forms a *picrate*, m. p. 123—125°. 7-*Methyl*-2-*ethyltetrahydroindazole*, a colourless oil, b. p. 108·5°/10 mm., gives a *picrate*, m. p. 101—102°, and a *methiodide*, m. p. 102—103°, the latter affording 7-methyl-2-ethyltetrahydroindazole when heated. 7-*Methyl*-2-*benzyltetrahydroindazole*, a colourless oil, b. p. 181—183°/12 mm. or 152°/3 mm., forms a *methiodide* (leaflets, m. p. 175° [decomp.]), which is also obtained from 2 : 7-dimethyltetrahydroindazole and benzyl iodide, and, on heating, affords the two last-named substances. The fact that the 7-methyl group prevents alkylation in position 1 is to be ascribed to electrochemical (not

stereochemical) effects (cf. attempts to prepare 1 : 5-dialkylpyrazoles by Auwers and Broche, A., 1923, i, 151).

The formation of quaternary salts from the reduced indazoles is not altogether parallel to their formation in the ordinary series. The 2-methyl- and 2-ethyl-tetrahydroindazoles follow the general rule. Methyl iodide converts either 1- or 2-methyltetrahydroindazole into 1 : 2-*dimethyl*-4 : 5 : 6 : 7-*tetrahydroindazolium iodide* (m. p. 152—153°). Ethyl iodide converts either 1- or 2-ethyltetrahydroindazole into 1 : 2-*diethyltetrahydroindazolium iodide* (m. p. 98—99°). Since these quaternary salts afford mixtures of 1- and 2-alkyl derivatives when heated, they are given formulæ V or VI, or, better, VII :



(V.)



(VI.)

$[C_6H_8\cdot CH(N^2R)(N^1R)]I.$ (VII.)

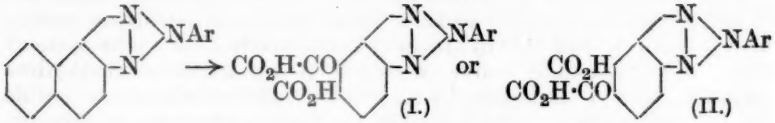
2-Benzyltetrahydroindazole, when heated with ethyl iodide, affords the *compound* (m. p. 138—139°) obtained by heating 2-ethyltetrahydroindazole with benzyl iodide. The compound, on heating, affords pure 2-ethyltetrahydroindazole, and therefore is written as $[C_6H_8\cdot CH(N^2Et[Ph\cdot CH_2\cdot])(N^1)]I$, both alkyl groups being attached to the same nitrogen atom. Similarly, the *compound*, $[C_6H_8\cdot CH(N^2)(N^1Et[Ph\cdot CH_2\cdot])]I$ (m. p. 127—128°), is formed from 1-benzyltetrahydroindazole and ethyl iodide or from the 1-ethyl derivative and benzyl iodide. The 1 : 1-quaternary salt, on heating, affords, not 1-ethyl-, but 2-ethyl-tetrahydroindazole.

7-Methyltetrahydroindazole gives quaternary salts in which the two alkyl groups are attached to the same nitrogen atom (see *ante*). The *methiodides* of 1- and 2-phenyltetrahydroindazoles afford, when heated, the parent phenyl derivatives.

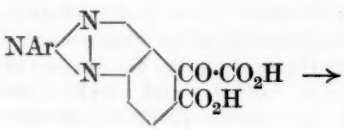
7-Methyltetrahydroindazole reacts with ethyl bromoacetate to give *ethyl* 7-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazyl*-2-*acetate* (colourless oil, b. p. 166·5—167·5°/14 mm.; *picrate*, m. p. 127—130° [indef.]). The corresponding *acid* (also obtainable from the indazole and chloroacetic acid), obtained by hydrolysis, forms white needles, m. p. 168—169° (*silver* salt described), and has, unlike the indazole bases, a sweet taste. E. E. T.

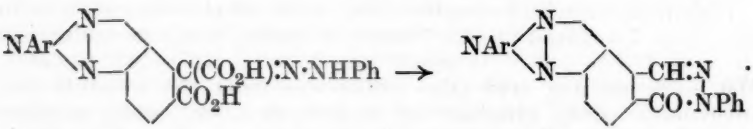
***vic.*-2 : *N*-Aryltriazolephthalonic Acids.** G. CHARRIER (*Gazzetta*, 1923, **53**, 829—843).—It has been shown by Dimroth (A., 1902, i, 403) that, starting from the three isomeric *N*-phenyl derivatives of 1 : 2 : 3-triazolemonocarboxylic acid and eliminating the phenyl group by oxidation after nitrating and converting into the amino-derivative by reduction, one and the same acid is obtained; the desmotropy of the triazole ring is thus established. Oxidation of naphthalene by means of alkaline permanganate solution yields mainly phthalonic acid, and the author finds similarly that the 2-arylnaphthatriazoles give, under the same

conditions, principally the corresponding vicinal 2-aryltriazole-phthalonic acids,



Since these acids are highly stable towards oxidising agents and are prone to form monometallic salts with the alkali metals, probably owing to the formation of an internal anhydride between the $\cdot CO \cdot CO_2H$ group and the triazole ring, and further on account of the analogy existing between them and the product of the oxidation of naphthalic acid by permanganate in alkaline solution (cf. Graebe and Bossel, A., 1893, i, 593), formula (I) is regarded as preferable to formula (II). The constitution of these acids is shown also by their oxidation to the corresponding 2-aryltriazolephthalic acids (annexed formula), and by their ability to react as keto-acids, analogously to phthalonic acid, with phenylhydrazine hydrochloride to form phenylhydrazones. The latter are far more stable than those of phthalonic acid, since only by heating above their melting points are they transformed, like phenylhydrazones of a keto-acid, into derivatives of the corresponding ketotetrahydropyridazines (pyridazinones); a carboxyl group is eliminated at the same time, so that from a dibasic acid a neutral heterocyclic derivative is obtained :





These acids behave as comparatively strong dibasic acids; they decompose carbonates, form well crystallised salts containing water of crystallisation, and readily yield normal and acid esters and amides. When subjected to prolonged energetic oxidation, they give the corresponding phthalic acids.

[With A. Odifreddi, A. Manfredi, and E. Mars.]—*vic.-2-Phenyltriazolephthalonic acid*, $C_{15}H_9O_5N_3$, obtained by oxidising 2-phenylnaphthatriazole, crystallises in white or lustrous needles, m. p. 242°, and has an intense acid reaction towards litmus, methyl orange and phenolphthalein. It yields the following derivatives: *monosodium* salt, $C_{15}H_8O_5N_3Na,4H_2O$, m. p. 324—325°, gives aqueous solutions acid to litmus and phenolphthalein. The normal

barium salt crystallises with $4H_2O$ and also with $5H_2O$, and when subjected to dry distillation in the anhydrous state yields *vic.*-2-*phenyltriazolephthalic anhydride* (annexed formula), which crystallises in slender, white needles, m. p. 183—184°, and, when treated with *m*-diethylaminophenol and zinc chloride, gives a deep red, crystalline colouring matter; the hydrochloride of the latter dissolves in boiling alcohol to an intense reddish-violet, markedly fluorescent solution, and crystallises in slender, metallic green needles similar to the crystals of rhodamine base B hydrochloride. *Basic barium* 2-*phenyltriazolephthalonate*, $\left[PhN_3{:}C_6H_2{<}\begin{matrix}CO{\cdot}CO_2\\CO_2\end{matrix}{>}Ba\right]_3,Ba(OH)_2,12H_2O$, forms rosettes of slender, silky needles and decomposes before melting. The *strontium* salt, $C_{15}H_{17}O_5N_3Sr,4\frac{1}{2}H_2O$, forms lustrous, white needles and decomposes before melting. The *methyl* ester, $C_{13}H_7ON_3(CO_2Me)_2$, forms minute, white prisms, m. p. 87—88°, and the *methyl hydrogen* ester, $C_{16}H_{11}O_5N_3$, colourless, prismatic crystals, m. p. 201—202°. The *ethyl* ester crystallises in colourless prisms, m. p. 169—170°. The *diamide*, $C_{13}H_7ON_3(CO{\cdot}NH_2)_2$, forms lustrous, colourless prisms, m. p. 233—234°, and, when boiled with 10% ammonia solution, yields the *ammonium* salt of the *monoamide*, $C_{15}H_{13}O_4N_5$, which crystallises in slender, white needles, m. p. 250° (decomp.). The *phenylhydrazone*, probably

$$Ph{\cdot}N_3{:}C_6H_2(CO_2H){\cdot}C(CO_2H){:}N{\cdot}NHPh,$$

crystallises in white, silky needles, m. p. 206—207° (decomp.), and acts as an energetic acid.

The monocarboxylic ketotetrahydropyridazinic acid, that is, the pyridazinone of *vic.*-2-phenyltriazolephthalonic acid, is not formed when the phenylhydrazone is boiled in acetic acid, but when heated at 250° the phenylhydrazone loses carbon dioxide and water, to give the decarboxylated *pyridazinone* (annexed formula), which crystallises in colourless prisms, m. p. about 200°. When the phenylhydrazone is treated in boiling water with barium carbonate, phenylhydrazine separates and the pentahydrated normal *barium* 2-*phenyltriazolephthalonate*, $C_{15}H_7O_5N_3Ba,5H_2O$, and the *dodecahydrated basic barium* salt,

$$C_{45}H_{21}O_{15}N_9Ba_3,Ba(OH)_2,12H_2O,$$

are formed.

The great resistance offered by *vic.*-2-phenyltriazolephthalonic acid to oxidising agents may be due to the existence of an anhydridic linking between the triazole nucleus and the ·CO·CO_2H group, which is thus protected from the action of nascent oxygen. The acid is, however, attacked by chromic acid with formation of a *compound* which crystallises in aggregates of radiating leaflets, m. p. 250°, acts as an energetic acid, and has the nitrogen content of a *vic.*-2-phenyltriazolephthalic acid.

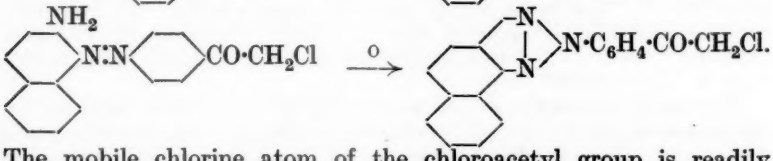
vic.-2-p-*Chlorophenyltriazolephthalonic acid*, $C_6H_4Cl\cdot N_3{:}C_6H_2(CO_2H)\cdot CO\cdot CO_2H$, crystallises in slender, white needles, m. p. 264—265°; its *monosodium* salt ($+2H_2O$) does not melt at 360°.

2-p-*Bromophenylnaphthatriazole*, $C_{10}H_6\cdot N_3\cdot C_6H_4Br$, prepared by oxidising *p*-bromophenylazo-β-naphthylamine by means of chromic acid in acetic acid solution, crystallises in white, silky needles, m. p. 200°.

vic.-2-p-*Bromophenyltriazolephthalonic acid*, obtained by the action of alkaline permanganate solution on the preceding compound, forms flat, white needles, m. p. 270°; its *monosodium* salt ($+2H_2O$) does not melt at 320°.

vic.-2-p-*Carboxyphenyltriazolephthalonic acid*, $C_{16}H_9O_7N_3$, crystallises in slender, white needles, m. p. 287—288° (decomp.), and is an energetic tribasic acid; its *monosodium* salt ($+4\frac{1}{2}H_2O$) does not melt at 350°. T. H. P.

αβ-Naphthatriazoles. G. CHARRIER and M. GALLOTTI (*Gazzetta*, 1923, **53**, 851—861).—The authors have prepared 2-*p*-chloroacetylphenyl-αβ-naphthatriazole by means of the following series of reactions: $Ph\cdot NHAc \rightarrow CH_2Cl\cdot CO\cdot C_6H_4\cdot NHAc \rightarrow CH_2Cl\cdot CO\cdot C_6H_4\cdot NH_2 \rightarrow CH_2Cl\cdot CO\cdot C_6H_4\cdot N_2Cl + C_{10}H_7\cdot NH_2 \rightarrow$



The mobile chlorine atom of the chloroacetyl group is readily replaced, giving the corresponding iodo- and cyano-derivatives. Hydrolysis of the latter gives the unstable ketonic acid, which loses carbon dioxide to form the corresponding ketone, 2-*p*-acetylphenyl-αβ-naphthatriazole. Treatment of the chloroacetyl compound with silver acetate yields the acetyl derivative of the corresponding ketocarbinol, αβ-naphthatriazole-2-*p*-benzoylcarbinol, which may be obtained either by hydrolysis of the acetyl derivative or by the action of moist silver oxide on the chloroacetyl compound itself. The latter reacts normally with ammonia, yielding αβ-naphthatriazole-2-*p*-benzoylmethylamine, whilst with primary aliphatic amines both substitution and addition occur, the unstable compound thus formed losing water and alkylamine when treated with an acid or even with a solvent:

$$C_{10}H_6{:}N_3\cdot C_6H_4\cdot CO\cdot CH_2Cl \rightarrow C_{10}H_6{:}N_3\cdot C_6H_4\cdot CO\cdot CH_2\cdot NHR, xNH_2R \rightarrow C_{10}H_6{:}N_3\cdot C_6H_4\cdot C(:NR)\cdot CH_2\cdot NHR;$$

the resulting compound consists of the corresponding 2-*p*-β-alkylamino-α-alkyliminoethylphenyl-αβ-naphthatriazole. Aniline acts similarly to ammonia, the chlorine atom of the *p*-chloroacetyl group being replaced by the anilino residue.

[With R. SALA, Q. MINGOIA, and P. TORAZZI.]—p-*Chloroacetylbenzeneazo-β-naphthylamine*, $NH_2 \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_4 \cdot CO \cdot CH_2Cl$, crystallises in thin, lustrous, garnet-red leaflets, m. p. 172°, and dissolves in concentrated sulphuric acid to a magenta-red solution. Its *phenylhydrazone* forms a red, crystalline powder with metallic green reflex, m. p. 180° (decomp.).

2-p-*Chloroacetylphenyl-αβ-naphthatriazole*,

$$C_{10}H_6 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle N \cdot C_6H_4 \cdot CO \cdot CH_2Cl,$$

prepared by oxidising the preceding compound by means of chromic acid, forms thin, white leaflets, m. p. 198°, and dissolves in concentrated sulphuric acid to a yellow solution. Its *phenylhydrazone* crystallises in thin, pale yellow leaflets, m. p. 156°.

2-p-*Iodoacetylphenyl-αβ-naphthatriazole* separates in lustrous, white needles, m. p. 195°.

2-p-*Cyanoacetylphenyl-αβ-naphthatriazole*, $C_{19}H_{12}ON_4$, crystallises in slender, yellow needles, m. p. 185°, with previous contraction, and, on protracted boiling with 50% sulphuric acid, gives 2-*p*-acetylphenyl-αβ-naphthatriazole (cf. A., 1922, i, 771).

αβ-*Naphthatriazole*-2-p-*benzoylcarbinol*,

$$C_{10}H_6 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle N \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot OH,$$

crystallises in silvery leaves, m. p. 191°, and its *acetyl* derivative in slender, white needles, m. p. 187°.

αβ-*Naphthatriazole*-2-p-*benzoylmethylamine*,

$$C_{10}H_6 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle N \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NH_2,$$

forms minute, almost colourless crystals, m. p. 192°, and gives a pale yellow *hydrochloride*, m. p. 184°.

2-p-β-*Methylamino-α-methyliminoethylphenyl-αβ-naphthatriazole*, $C_{10}H_6 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle N \cdot C_6H_4 \cdot C(:NMe) \cdot CH_2 \cdot NHMe$, crystallises in yellow needles, m. p. 160°, and forms a yellowish-brown hydrochloride.

2-p-β-*Ethylamino-α-ethyliminoethylphenyl-αβ-naphthatriazole*, $C_{22}H_{23}N_5$, separates in slender, pale yellow needles, m. p. about 150° with previous contraction.

αβ-*Naphthatriazole*-2-p-*benzoylmethylaniline*,

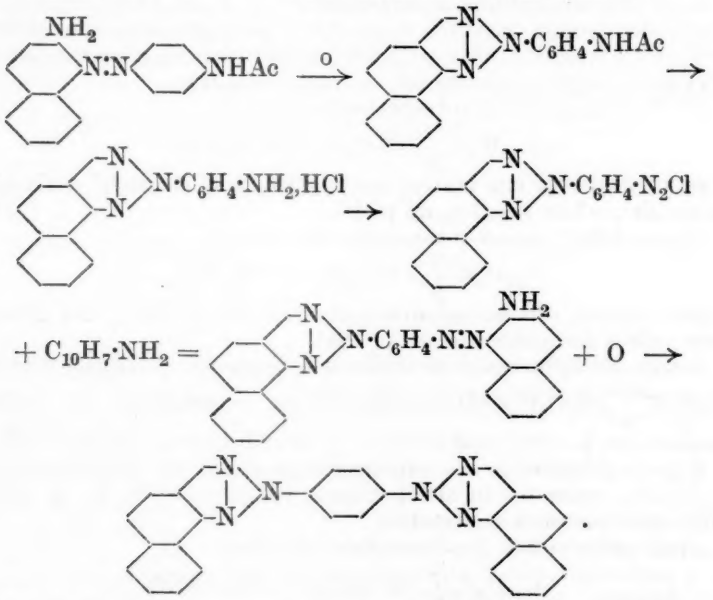
$$C_{10}H_6 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle N \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NHPh,$$

crystallises in lustrous, sulphur-yellow leaflets, m. p. 277°, and forms benzene solutions exhibiting pronounced greenish-yellow fluorescence; its *phenylhydrazone* separates in slender, lemon-yellow needles, m. p. about 270° (decomp.). T. H. P.

Oxidation of Uric Acid by Iodine in Alkaline Solution. J. MORE (*Compt. rend.*, 1924, **178**, 498—501).—Oxidation of uric acid (1 mol.) by iodine (2 atoms), in potassium hydrogen carbonate solution, affords a substance (not isolated), which is converted by acetic acid into allantoin, and (cf. Biltz and Max, A., 1921, i, 893) is further oxidisable by iodine in acid solution. Oxidation

of uric acid by means of iodine in sodium hydroxide solution (cf. Kreidl, A., 1893, ii, 558) gives first a substance which affords a uroxanate on evaporation in alkaline solution, or allantoin on evaporating in acetic acid solution, and in presence of alkali may also pass into a less readily oxidised isomeride. The latter, however, yields the same products as above, on evaporation in alkaline or acid solution, and on oxidation with iodine gives *allantoxalic amide*. The latter, when treated with concentrated potassium hydroxide, affords potassium allantoxalate; the following *salts* are described: $C_4H_3O_3N_4K,1{\cdot}5H_2O$; $C_4H_3O_3N_4Na,1{\cdot}5H_2O$, and $C_4H_3O_3N_4(NH_4),H_2O$. E. E. T.

***p*-Phenylene-1:2-dinaphthaditriazole.** G. CHARRIER (*Gazzetta*, 1923, **53**, 862—867).—This compound has been prepared by means of the following series of reactions: $C_6H_5{\cdot}NHAc \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NHAc \longrightarrow NH_2{\cdot}C_6H_4{\cdot}NHAc \longrightarrow N_2Cl{\cdot}C_6H_4{\cdot}NHAc + C_{10}H_7{\cdot}NH_2 \longrightarrow$



It is a highly stable compound and, as is usual with αβ-naphthatriazoles, is oxidised by permanganate in alkaline solution, giving *vic.*-*p*-phenyleneditriazolediphthalonic acid. Derivatives of the *p*-phenylene-1 : 2-dinaphthaditriazole have not previously been prepared (cf. Morgan and Chazan, A., 1922, i, 181). It is found possible to pass directly, by oxidation by means of alkaline permanganate solution, from 1 : 2-naphthatriazole-2-*p*-benzeneazo-β-naphthylamine to the above diphthalonic acid, preparation of the corresponding naphthatriazole as an intermediate product being unnecessary. Similarly, *vic.*-2-phenyltriazolephthalonic acid may be prepared directly from 1-benzeneazo-2-naphthylamine.

[With G. Bonomi and T. Bettinazzi.]—*p*-Acetylaminobenzeneazo-β-naphthylamine, $C_{18}H_{16}ON_4$, prepared by the interaction of *p*-acetylaminophenyldiazonium chloride and β-naphthylamine in alcoholic solution, crystallises in slender, orange-red needles, m. p. 208°.

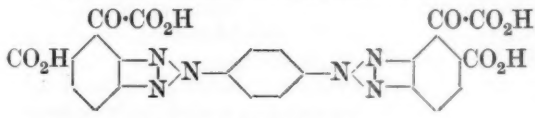
2-p-*Acetylaminophenyl*-1 : 2-*naphthatriazole*, $C_{18}H_{14}ON_4$, obtained by oxidising the preceding compound in acetic acid solution by means of chromic acid, forms slender, white needles, m. p. 228°, and exhibits marked blue fluorescence even in very dilute solutions.

2-p-*Aminophenyl*-1 : 2-*naphthatriazole*, $C_{16}H_{12}N_4$, crystallises in lustrous, silky, white needles, m. p. 200°.

1 : 2-*Naphthatriazole*-p-*benzeneazo*-β-*naphthylamine*, $C_{26}H_{18}N_6$, separates in bright red needles, m. p. 250°.

p-*Phenylene*-1 : 2-*dinaphthaditriazole*, $C_{26}H_{16}N_6$, forms thin, pink laminæ, m. p. 333°.

vic.-p-*Phenyleneditriazolediphthalonic acid* (annexed formula), crystallises in slender, white needles, m. p. 322—323°, with slight browning at 320°.



2-*Phenyltriazolephthalonic acid*, $Ph{\cdot}N_3{:}C_6H_2(CO_2H){\cdot}CO{\cdot}CO_2H$ [$N_3Ph : CO_2H : CO{\cdot}CO_2H = 12 : 4 : 3$], prepared by oxidising benzeneazo-β-naphthylamine by means of alkaline permanganate solution, crystallises in lustrous, white needles, m. p. 242°. T. H. P.

s-Trinitroarylazodiarylamines. A. Beretta (*Gazzetta*, 1923, **53**, 870—876).—By the action of picryl chloride on aminoazo-derivatives in alcoholic solution in presence of sodium acetate, the author has prepared the *s*-trinitrophenyl derivatives of various *o*-, *m*-, and *p*-aminoazo-compounds of the benzene and naphthalene series.

3′-*Benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $(NO_2)_3C_6H_2{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}NPh$, obtained from *m*-aminoazobenzene, crystallises in slender, yellow needles, m. p. 212°, and dissolves in concentrated sulphuric acid to a yellow solution. 4′-Benzeneazo-2 : 4 : 6-trinitrodiphenylamine (cf. Walther and Lehmann, A., 1904, i, 352) has m. p. 178°. 3′-*Methyl*-6′-p-*toluneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $C_6H_4Me{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_6H_2(NO_2)_3$, prepared from *p*-toluneazo-*p*-toluidine, forms slender, slightly orange, red crystals, m. p. 201°, and gives a red solution in concentrated sulphuric acid. 2′-*Methyl*-4′-*o*-*toluneazo*-2 : 4 : 6-*trinitrodiphenylamine* crystallises in red needles, m. p. 194°, and dissolves in concentrated sulphuric acid to a red solution. 3′-*Amino*-4′-*benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $C_{18}H_{13}O_6N_7$, prepared from 2 : 4-diaminoazobenzene (chrysoidine), forms minute, red crystals, m. p. 254° (decomp.), and gives a red solution in concentrated sulphuric acid. 3′-*Amino*-6′-*methyl*-4′-*benzeneazo*-

2 : 4 : 6-*trinitrodiphenylamine*, $C_{19}H_{15}O_6N_7$, prepared from 2 : 4-diaminoazomethylbenzene (methylchrysoidine), forms slender, lustrous prisms with metallic reflexion, m. p. 228° (decomp.), and dissolves in concentrated sulphuric acid to a red solution. 3′-*Acetylamino*-6′-*methyl*-4′-*benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine* crystallises in slender, orange-yellow prisms, m. p. 215° (decomp.). 3′-*Amino*-6′-*methyl*-4′-p-*chlorobenzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $C_{19}H_{14}O_6N_7Cl$, prepared from 4′-chloro-2 : 4-diamino-5-methylazobenzene, crystallises in slender, metallic brown prisms, m. p. 235° (decomp.), and forms a red solution in concentrated sulphuric acid. The corresponding 3′-*acetylamino*-compound separates in slender, orange crystals, m. p. 228° (decomp.). 3′-*Amino*-6′-*methyl*-4′-p-*bromobenzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*,

$$C_{19}H_{14}O_6N_7Br,$$

crystallises in slender, lustrous, brown needles, m. p. 233° (decomp.), and dissolves in concentrated sulphuric acid to a red solution. The corresponding *acetylamino*-derivative forms slender, orange needles, m. p. 227° (decomp.).

α-*Benzeneazo*-β-*naphthyl*-2 : 4 : 6-*trinitrophenylamine*,

$$Ph{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_2(NO_2)_3,$$

prepared from benzeneazo-β-naphthylamine, crystallises in slender, reddish-brown needles, m. p. 221° (decomp.), and dissolves in concentrated sulphuric acid to a blue solution. α_2-*Benzeneazo*-α_1-*naphthyl*-2 : 4 : 6-*trinitrophenylamine* forms slender, reddish-brown needles, m. p. 193° (decomp.), and yields a blue solution in concentrated sulphuric acid. T. H. P.

Studies in Dyes with Multiple Chromophores. R. N. Sen and B. Sett (*J. Amer. Chem. Soc.*, 1924, **46**, 111—119).—Three types of azo-triphenylmethane dyes have been studied containing, respectively, one, two, and three azo-groups in the *p*-position to the central carbon atom. It has been found that the introduction of one azo-group deepens the colour (compare T., 1912, **101**, 1113), of two azo-groups lightens the colour, and of three makes it still lighter. The effect of the multiplication of chromophores has also been studied by introducing simultaneously an azo-methine group and an azo-group into chrysoidine, rosaniline, safranine, and Congo-red, and in each case the colour becomes lighter. The direct-dyeing property of Congo-red also disappears. The introduction of the azo-group has been found to deepen the colour in the case of an indamine dye as well as in the case of fluorescein.

The preparation and properties of the following dyes, which appear to be new substances, are described: *phenetoleazosulphophenyltetramethyldiaminodiphenylcarbinol* (from phenetoleazobenzaldehydesulphonic acid and dimethylaniline) dyes wool green; *dimethylaminobenzeneazophenyltetramethyldiaminodiphenylcarbinol* (from benzeneazodimethylaniline and tetramethyldiaminobenzhydrol) dyes wool blue; *salicylylazophenyldisalicylylcarbinol* (from methylenedisalicylic acid and benzeneazosalicylic acid) dyes wool red; *phenyldi*(*dimethylaminobenzeneazophenyl*)*carbinol* (from benz-

aldehyde and benzeneazodimethylaniline) dyes wool violet; *phenetoleazosulphophenyldi(dimethylaminobenzeneazophenyl)carbinol* (from phenetoleazobenzaldehydesulphonic acid and benzeneazodimethylaniline) dyes wool yellow; *diphenetoleazosulphobenzylidenechrysoidine* (from chrysoidine hydrochloride and phenetoleazobenzaldehydesulphonic acid) dyes wool golden-yellow; *diphenetoleazosulphobenzylidene-rosaniline hydrochloride* (from rosaniline and phenetoleazobenzaldehydesulphonic acid) dyes wool bluish-red; *diphenetoleazosulphobenzylidene-safranine hydrochloride* (from safranine and phenetoleazobenzaldehydesulphonic acid) dyes wool red; *dimethylaminobenzeneazophenyldimethylquinoneimine hydrochloride* (from nitrosodimethylaniline hydrochloride and benzeneazodimethylaniline) dyes wool olive-green; *sulphobenzeneazofluorescein* (from diazotised sulphanilic acid and fluorescein) dyes wool orange.

F. A. M.

Amine Oxidation. VIII. Oxidation of Aliphatic Amines. S. GOLDSCHMIDT and V. VOETH (*Annalen*, 1924, **435**, 265—277).—Benzylamine is oxidised by potassium permanganate in aqueous or in acetone solution to give benzaldehyde, no intermediate compound being isolable even if oxidation be effected at −60°. Since, however, benzaldehyde, under similar conditions, is rapidly oxidised to benzoic acid, it cannot be the primary product in the oxidation of benzylamine, which probably proceeds thus: $PhCH_2{\cdot}NH_2 \rightarrow PhCH_2{\cdot}N: \rightarrow PhCH{:}NH \rightarrow PhCH{:}O + NH_3$.

Dibenzylamine is oxidised by permanganate in acetone solution to give *benzoyltribenzylhydrazine* (white needles, m. p. 181°), the constitution of which was established by synthesis (from tribenzoylhydrazine and benzoyl bromide); its formation is explained by the scheme: $2(PhCH_2)_2NH \rightarrow 2(PhCH_2)_2N: \rightarrow (PhCH_2)_2N{\cdot}N(CH_2Ph)_2 \rightarrow (PhCH_2)_2N{\cdot}NBz{\cdot}CH_2Ph$. Confirmation of this explanation was obtained: tetrabenzylhydrazine on oxidation with permanganate gives benzoyltribenzylhydrazine, which, on reduction with zinc dust and acetic acid, yields benzylbenzamide (and traces of benzaldehyde and dibenzylamine), and on treatment with mineral acids gives (per mol.) benzaldehyde (1 mol.) and *hydroxytribenzylhydrazine hydrochloride*. The latter (m. p. 220—240° [indef.]) could not be obtained in a pure state and was found to contain dibenzylamine hydrochloride, whilst, on treating it with alkali, benzamide and tribenzylhydrazine were isolated.

The oxidation of di-*n*-propylamine by means of permanganate gives αβ-*dipropionyl*-αβ-*di*-n-*propylhydrazine*,

$$COEt{\cdot}NPr^{\alpha}{\cdot}NPr^{\alpha}{\cdot}COEt.$$

This substance, evidently formed by the oxidation of the first-formed tetrapropylhydrazine, was only obtained in a slightly impure state as a yellow oil possessing an odour like that of menthol, and beginning to decompose at 40° (more readily in presence of alkali) with formation of propaldehyde. The dipropionyl derivative, on being distilled, affords a mixture of propaldehyde, n-*propylpropionamide*, $NHPr^{\alpha}{\cdot}COEt$ (pale yellow oil, b. p. 64—65°/

0·4 mm.), and n-*propylidenepropionamide*, CHEt:N·COEt (viscous, greenish-yellow oil, b. p. 87°/0·4 mm.).

Aqueous permanganate with piperidine gave no isolable products, but in acetone solution oxidation proceeded much more rapidly than in the cases described already, to give N-*piperidyl*-N-2-*piperidone* as a yellowish-red oil, which, on distillation, was converted into a mixture of tetrahydropyridine and 2-piperidone (b. p. 64—65°/0·4 mm.). E. E. T.

Certain Nitroarylhydrazines. M. Giua (*Gazzetta*, 1923, **53**, 844—851).—The results obtained when various aromatic nitro-compounds are treated with semicarbazide show that the latter serves to replace by the residue ·NH·NH·CO·NH_2, not only the nitro-group, but also labile halogen atoms. Thus, when heated on a water-bath in alcoholic solution containing sodium acetate, 1-chloro-2 : 4-dinitrobenzene and semicarbazide react in accordance with the equation: $C_6H_3Cl(NO_2)_2+2NH_2·NH·CO·NH_2=C_6H_3(NO_2)_2·NH·NH·CO·NH_2+NH_2·CO·NH·NH_2,HCl$. In the case of nitro-compounds containing a labile nitro-group, the formation of nitrous acid renders the reaction somewhat complicated, and, although the yields of nitrophenylsemicarbazides are good, various secondary products are also formed. With β- and γ-trinitrotoluenes the first phase of the reaction is probably expressed by the equation: $C_6H_2Me(NO_2)_3+2NH_2·NH·CO·NH_2=C_6H_2Me(NO_2)_2·NH·NH·CO·NH_2+NH_2·CO·N_3+2H_2O$; the azide of carbamic acid has not been observed among the secondary products, but small proportions of cyanuric acid, which is one of the many transformation products of this azide, have been detected (cf. Curtius and Schmidt, A., 1923, i, 1080).

4 : 6-*Dinitro*-m-*tolylsemicarbazide*, obtained by the action of semicarbazide on γ-trinitrotoluene, forms crystals, m. p. 237—238° (decomp.). 2 : 4-*Dinitro*-m-*tolylsemicarbazide*, similarly obtained from β-trinitrotoluene, forms crystals, m. p. 185° (decomp.), and in alcoholic solution yields a reddish-brown coloration with alkalis. 5-*Chloro*-2 : 4-*dinitrophenylsemicarbazide*, prepared from 1-chloro-2 : 4 : 5-trinitrobenzene, forms yellow crystals, m. p. 217—218° (decomp.). 2 : 4-*Dinitrophenylsemicarbazide*, $C_7H_7O_5N_5$, prepared from 1-chloro-2 : 4-dinitrobenzene, forms pale yellow crystals, m. p. 205—207° (decomp.).

α-*Methyl*-α-*phenyl*-5-*chloro*-2 : 4-*dinitrophenylhydrazine*, $Cl(NO_2)_2C_6H_2·NH·NMePh$, obtained by the interaction of *as*-methylphenylhydrazine and 1-chloro-3 : 4 : 6-trinitrobenzene, crystallises in orange-yellow lamellæ, m. p. 120—121°, and dissolves in concentrated sulphuric acid to a reddish-brown solution.

Acetone 4 : 6-*dinitro*-m-*tolylhydrazone*, $C_{10}H_{12}O_4N_4$, crystallises in yellow needles, m. p. 144—145°, and in alcoholic solution gives a dark red coloration with an alkali. Other 4 : 6-dinitro-*m*-tolylhydrazones are those of: *acetophenone*, $C_{15}H_{14}O_4N_4$, crystallising in orange-yellow needles, m. p. 215—216°; *ethyl phenyl ketone*, $C_{16}H_{16}O_4N_4$, forming a red, crystalline powder, m. p. 183—184°;

benzaldehyde, $C_{14}H_{12}O_4N_4$, crystallising in reddish-yellow needles, m. p. 224—225°; *anisaldehyde*, separating in garnet-red prisms, m. p. 238—239° (decomp.); p-*tolualdehyde*, $C_{15}H_{14}O_4N_4$, forming lustrous, deep red needles, m. p. 237—238°; *cinnamaldehyde*, $C_{16}H_{14}O_4N_4$, forming bright red needles, m. p. 263—264° (decomp.). T. H. P.

Additive Reactions of the Phosphorus Halides. VIII. Kinetic Evidence in Regard to the Mechanism of the Reaction. J. B. CONANT and V. H. WALLINGFORD (*J. Amer. Chem. Soc.*, 1924, **46**, 192—202; cf. A., 1923, i, 498).—The reaction between benzaldehyde and phosphorus trichloride proceeds to a definite equilibrium both in the absence of a solvent and in benzene solution. The composition of the equilibrium mixture accords with the law of mass action. An earlier explanation of the mechanism of the reaction between carbonyl compounds, phosphorus trichloride, and acetic acid or anhydride assumed that this addition reaction was an intermediate step; this explanation is now abandoned. The gradual addition of small amounts of water to a mixture of benzaldehyde and the trichloride causes an irreversible reaction to take place. The product appears to be an open-chain phosphorus compound which readily loses hydrogen chloride to form a phostonic acid derivative (cf. Conant and Macdonald, A., 1921, i, 69). The reaction between a trichloride, an aldehyde, and acetic acid must be either a direct interaction of three molecules or a reaction in which some open-chain additive product of an unstable nature is an intermediate; the authors favour the latter alternative. F. A. M.

Action of Halogen Derivatives of Phosphorus on some Phenolic Bases. M. BOURNEUF (*Bull. Soc. chim.*, 1923, **33**, [iv], 1808—1823).—When dimethylaniline (2 mols.) is heated at 70° with phosphorus trichloride (1 mol.), *p*-dimethylaminophenyldichlorophosphine, $NMe_2 \cdot C_6H_4 \cdot PCl_2$, is primarily formed, since sodium carbonate converts the product into a mixture (with dimethylaniline) of *tetramethyldiaminodiphenylphosphine oxide*, $(NMe_2 \cdot C_6H_4)_2PHO$, m. p. 169° (insoluble), and dimethylaminophenylphosphinic acid (soluble, and stable towards boiling water; cf. Michaelis and Schenk, A., 1888, 834). The above oxide, in presence of water and air, gives tetramethyldiaminodiphenylphosphinic acid (m. p. 249—250° on Maquenne block, or 199° [decomp.] in capillary tube), the latter being formed, together with *hexamethyltriaminotriphenylphosphine dihydroxide*, $(NMe_2 \cdot C_6H_4)_3P(OH)_2$, (m. p. 321° on Maquenne block) in the original condensation.

Diethylaniline and phosphorus trichloride give non-crystalline products.

Dimethylaniline (4 mols.), when heated with 1 mol. of phosphorus oxychloride at 130°, the product then being treated with sodium hydroxide, gives a mixture of (1) tetramethyldiaminodiphenylphosphinic acid, affording dimethylaniline when heated with calcium carbonate or with mineral acids; *sodium* salt,

$$(NMe_2 \cdot C_6H_4)_2P(ONa):O,H_2O;$$

(2) tetramethyldiaminodiphenylmethane, and (3) *hexamethyltriaminotriphenylphosphine oxide*, m. p. 262°, and the corresponding hydroxide (cf. *supra*).

Diethylaniline is converted by phosphorus oxychloride into *tetraethyldiaminodiphenylphosphinic* acid (m. p. 195° [decomp.] or 253—254° on Maquenne block), which is decomposed on heating with calcium carbonate or with mineral acids to give diethylaniline; it forms a *dihydrochloride* (hygroscopic, m. p. 185° on Maquenne block), a *sodium* salt (crystallising with 6 or $7H_2O$), and a *barium* salt.

Orthophosphoric acid and aniline give only aniline pyrophosphate.

E. E. T.

Studies Concerning the Direct Preparation of Organoberyllium Halides. H. GILMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2693—2695).—Metallic beryllium, even when freshly cleaned by treatment with very dilute pure nitric acid, does not react with methyl iodide, ethyl iodide, benzyl bromide, bromobenzene, chlorobenzene, or α-bromonaphthalene, using as solvents anhydrous ether, anisole, benzene, or β-ethoxynaphthalene, and as catalysts iodine, bromine, dimethylaniline, ethyl acetate, or freshly prepared Grignard reagent. Experiments in which freshly sublimed beryllium iodide was used, and one in which the reaction mixture was exposed to *X*-rays, were also unsuccessful. W. S. N.

Action of Polyhalogenated Derivatives of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. III. R. BINAGHI (*Gazzetta*, 1923, **53**, 879—887; cf. A., 1922, i, 313, 1002).—Towards magnesium ethyl bromide, tetrachloromethane behaves similarly to chloroform, giving only ethylene and methane. With magnesium phenyl bromide, however, it yields, not tetraphenylmethane, but hexaphenylethane, triphenylmethyl peroxide, and triphenylcarbinol. This reaction exhibits marked analogy to the formation of hexaphenylethane by the action of zinc on triphenylchloromethane (cf. Gomberg, A., 1901, i, 77, 638; 1913, i, 259), which is yielded by the first phase of the reaction $3MgPhBr+CCl_4=CPh_3Cl+3MgBrCl$. The latter compound then reacts with another molecule of magnesium phenyl bromide, giving hexaphenylethane and bromobenzene, which also occurs among the products of the reaction $2CPh_3Cl+MgPhBr=MgCl_2+PhBr+CPh_3{\cdot}CPh_3$. That the reaction proceeds thus is confirmed by the simultaneous formation of triphenylcarbinol, which, under the experimental conditions employed, could not arise except by the hydrolysis of the triphenylchloromethane either by the water added to precipitate the basic magnesium salt or by the current of steam used to remove the bromobenzene and diphenyl. Atmospheric oxidation of hexaphenylethane explains the formation of triphenylmethyl peroxide, which is not obtained when an atmosphere of hydrogen is employed.

In the reaction between magnesium ethyl bromide and tetrachloromethane, the first phase consists of the addition of four molecules of the magnesium alkyl compound to one molecule of the methane derivative, evolution of gases occurring only when

the product of the reaction is either left for some time or heated: $CCl_4+4MgEtBr=4MgClBr+4C_2H_4+CH_4$.

Triphenylmethyl peroxide, $O{:}O(CPh_3)_2$, forms a lustrous, white, microcrystalline powder, m. p. 186°, and yields rather low values for the molecular weight in freezing naphthalene. By dissolution in cold, concentrated sulphuric acid and subsequent addition of the solution to ice, triphenylcarbinol is obtained. Its *hexanitro*-derivative, $O{:}O[C(C_6H_4{\cdot}NO_2)_3]_2$, has m. p. 208—210°. T. H. P.

Arsino-arylamino-alcohols. C. W. Rodewald and R. Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 3102—3105).—Amino-arylarsinic acids on condensation with β-chloroethyl and γ-chloropropyl chloroformates yield ω-chloroalkyl-(arsino-aryl)carbamates. On treatment with two molecular equivalents of aqueous alkali, the β-chloroethyl compounds are converted into arsino-aryl oxazolidones and the γ-chloropropyl compounds into 3-arsino-aryl-tetrahydro-1 : 3 : 2-oxazones. Excess of alkali hydrolyses the oxazolidones to β-arsino-aryl amino-ethanols and the oxazones to γ-arsino-aryl-aminopropanols. *β-Chloroethyl* (p-*arsinophenyl*)*carbamate*,

$$C_6H_4(AsH_2O_3)NH{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2Cl,$$

has m. p. above 250°, the corresponding (o-*arsinophenyl*)*carbamate* having m. p. 156—157°. *β-Chloroethyl* (2-*methyl*-5-*arsinophenyl*)*carbamate* has m. p. 193—195°. The *γ-chloropropyl* (p-*arsinophenyl*)*carbamate*, $C_6H_4(AsH_2O_3)NH{\cdot}CO_2{\cdot}[CH_2]_3{\cdot}Cl$, and the corresponding o-*arsinophenylcarbamate* melt at 245—246° and 130—132°, respectively. *γ-Chloropropyl* (2-*methyl*-5-*arsinophenyl*)*carbamate* has m. p. 160—162°. 3-p-*Arsinophenyl*-2-*oxazolidone*, $C_6H_4(AsH_2O_3){\cdot}N{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2$, forms colourless plates, m. p. above 280°.

3-o-*Arsinophenyl*-2-*oxazolidone* crystallises in colourless plates, m. p. 212—213°. 3-p-*Arsinophenyl*-1 : 3 : 2-*oxazone*,

$$C_6H_4(AsH_2O_3){\cdot}N{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2,$$

crystallises in white plates, m. p. 245—247°. β-(p-*Arsinophenyl*)-*aminoethanol*, $C_6H_4(AsH_2O_3)NH{\cdot}CH_2{\cdot}CH_2OH$, has m. p. 173—174°; the corresponding o-*arsinophenyl* derivative has m. p. 144—146°. β-(2-*Methyl*-5-*arsinophenyl*)*aminoethanol* has m. p. 144—146°. γ-(p-*Arsinophenyl*)*aminopropanol* has m. p. 167—168°; the similar o-*arsinophenyl* compound has m. p. 84—85°. γ-(2-*Methyl*-5-*arsinophenyl*)*aminopropanol* melts at 142—143°. p-*Arsinophenyl*-β-*hydroxyethyl nitrosoamine*, $C_6H_4(AsH_2O_3)N(NO){\cdot}CH_2{\cdot}CH_2OH$, is obtained from the corresponding aminoethanol and nitrous acid. It crystallises in bright yellow needles, m. p. 236°. p-*Arsinophenyl*-γ-*hydroxypropyl nitrosoamine*, $C_6H_3(AsH_2O_3)N(NO)CH_2{\cdot}CH_2{\cdot}CH_2OH$, is prepared similarly. It forms yellow crystals, m. p. 142—143°. The arsino-aryl-amino-alcohols are much less toxic than the corresponding arsanilic acids. F. G. P.

The Protein Matter of Bile. J. F. Logan (*J. Biol. Chem.*, 1923, **58**, 17—32).—Attempts have been made by various methods to isolate a pure protein from ox bile, and elementary analyses have been made of several of the preparations obtained. The

results, however, indicate that, in each case, the product was probably a mixture of glucoprotein with a small amount of nucleoprotein. Direct acid hydrolysis did not liberate a reducing carbohydrate, but when this followed preliminary treatment with alkali the product had slight reducing properties. E. S.

Proteins of Wheat Bran. I. Isolation and Elementary Analyses of a Globulin, Albumin, and Prolamine. D. B. JONES and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1923, **58**, 117—131).—Wheat bran, as free as possible from other portions of the wheat kernel, has been found to contain 17·25% of protein ($N \times 6{\cdot}25$). By extracting the bran successively with water, 4% sodium chloride, 70% alcohol, and 0·5% sodium hydroxide, 86·61% of the total protein has been removed and an albumin, a globulin, and an alcohol-soluble protein (prolamine) have been isolated from the first three extracts. Elementary analyses gave the following results: albumin, C=53·21, H=6·71, N=15·42, S=1·35%; globulin, C=53·43, H=7·40, N=17·76, S=0·91%; prolamine, C=54·25, H=6·75, N=15·35, S=1·35%. E. S.

Theory of Vegetable Tanning. II. Dehydration of the Gelatin Sol by Tannic Acid, Crystalline Tannins, and Simpler Phenols. H. G. B. DE JONG (*Rec. trav. chim.*, 1924, **43**, 35—67; cf. A., 1923, i, 821).—The stability of a gelatin sol is governed by two factors, electric charge and hydration. At the isoelectric point, $p_H = 4{\cdot}7$, the gelatin sol is uncharged, but retains its stability above the gelation temperature (about 40°) on account of its hydration. Increase of the hydrogen-ion concentration causes the particles to assume a positive charge, up to a maximum, beyond which the charge decreases. In the same way, decrease of the hydrogen-ion concentration imparts a negative charge to the particles up to a point, beyond which discharge takes place. Isoelectric or discharged sols can be coagulated by addition of dehydrating substances such as alcohol. Hydration changes in a sol can be followed by viscosity measurements, although the charge can also influence the viscosity (the quasi-viscous effect). This view of gelatin sols, it is claimed, expresses their behaviour better than the view which regards them as ion disperse systems.

It is shown by viscosimetric measurements that gelatin sols at 40° obey Poiseuille's law, and that the viscosity minimum is situated, at 40°, at the isoelectric point. The effect of tannic acid and phenols on gelatin sols was studied viscosimetrically at this temperature at different hydrogen-ion concentrations. At a small concentration of hydrochloric acid (0·003*N*), tannic acid has a marked dehydrating action, indicated by a lowering of the viscosity, but no precipitation occurs. At the isoelectric point tannic acid has both a dehydrating and a positive charging action on account of its own slight acidity. Consequently the viscosity minimum of a gelatin sol containing tannic acid lies at a small nominal concentration of alkali, which serves to restore the medium to the p_H of the isoelectric point. Further addition of alkali causes a powerful

rehydration. The dehydration is relatively greatest at the isoelectric point, and, if pushed far enough, causes coagulation. The primary action of tannic acid on gelatin sols is therefore the same as on agar sols (*loc. cit.*). Phenol, pyrocatechol, resorcinol, quinol, pyrogallol, phloroglucinol, and ethyl gallate all have a similar dehydrating action on gelatin sols, the dehydrating action increasing rapidly with the number of phenolic groups. In the case of the two crystalline tannins, *d*-catechin and hamameli tannin, the dehydration is more powerful than with the simpler phenolic compounds. In the case of digalloylglucose, however, the positively charging influence of the tannin, tending to increase the viscosity, exceeds the dehydrating action, tending to lower the viscosity, at the isoelectric point, so that the viscosity is actually raised. However, a little sodium hydroxide in this case causes complete coagulation. Picric acid added to an isoelectric gelatin sol exerts at first a positively charging action, but with greater concentrations dehydration becomes very powerful, the positively charging action decreases, and finally precipitation occurs. Sodium picrate has no dehydrating action. E. H. R.

Gradual Decomposition of Proteins. Partial Hydrolysis of Keratin (Hog Bristles). E. Abderhalden and E. Komm (*Z. physiol. Chem.*, 1924, **132**, 1—11).—Hog bristles (400 g.) were heated with 1% hydrochloric acid (2 litres) in an autoclave at 120° for five hours, the product was neutralised with ammonia and then evaporated to dryness, mixed with sand and extracted with ethyl acetate. From the extract there were obtained *d*-alanylglycine anhydride, m. p. 250° (decomp.); prolyl-leucine anhydride, m. p. 158°, $[\alpha]_D^{20}$ −46·3° (in alcohol) (apparently partly racemised); *l-prolyl-d-valine anhydride*, m. p. 250—252°, and a *compound*, $C_{14}H_{23}O_3N_3$, m. p. 180—182°, which yields, on hydrolysis, proline, leucine, and alanine, and is formed from these by the loss of 3 mols. of water. From the product of the hydrolysis of hog bristles, using 70% sulphuric acid for seven days, the only pure compound isolated was *l-leucylserine*, $[\alpha]_D^{21}$ −44·3° (in water), and from the product of the hydrolysis by 70% sulphuric acid for fourteen days, a *valylvaline*, m. p. 255—260°, $[\alpha]_D^{20}$ +3·5° (in water), was obtained. In both cases, however, other scission products were shown to be present. W. O. K.

Biochemistry.

Iron Content of the Blood and Spleen in Infectious Equine Anæmia. L. H. Wright (*J. Agric. Res.*, 1923, **26**, 239—242).—Analyses of the blood and spleens of a number of normal and anæmic animals are given. It would appear that the average total of the solids—iron, hæmoglobin, and erythrocytes—is considerably greater in the case of normal horses. Anæmia is indicated

more by a lack of iron, and therefore of hæmoglobin, than by the number of erythrocytes. The increased iron content of the spleens of young horses is not considered to be entirely due to the larger amount of blood in the organ. A. G. P.

Relation between the Phosphate in Blood and Urine. V. B. WIGGLESWORTH and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, **B**, **95**, 558—570).—After the ingestion of acid or of alkaline sodium phosphate containing 1·5—2 g. of phosphorus, there is a 50—60% increase in the phosphate content of the blood, and simultaneously a large increase in the urinary phosphate. The urinary excretion of phosphorus is roughly proportional to the excess of phosphate above a certain value in the blood. Little change in the rate of excretion of phosphorus is caused by large variations in the amount of water excreted. The plasma and corpuscles normally contain equal amounts of inorganic phosphate, but when the phosphate in the whole blood is increased, that in the plasma exceeds that in the corpuscles. The organic fraction of the acid-soluble phosphorus does not increase after phosphate ingestion, or after ingestion of glucose with or without phosphate. W. O. K.

Some Experiments and Remarks on the Possible Transformation of *d*-Glucose in the Intestine and on the Nature of the Blood-sugar. S. VAN CREVELD (*Biochem. J.*, 1923, **17**, 860—871).—In agreement with Stiven and Reid (A., 1923, i, 1153), the observations of Hewitt and Pryde (A., 1920, i, 648) have not been confirmed. Using the aqueous humour of the eye and the blood-serum ultra-filtrate, it is shown that, although the former fluid when freshly collected decolorises potassium permanganate, neither fluid shows any mutarotation, and the copper-reducing value and the rotatory power are in close correspondence. In general, from the author's observations, no experimental support is forthcoming for the view that "reactive" sugars are intermediate metabolites, but the view that such may possibly occur is not abandoned. J. P.

The Absence of Effect of Insulin on the Heat Production in Isolated Frog's Muscle. R. AZUMA and W. HARTREE (*Biochem. J.*, 1923, **17**, 875—877).—Insulin has no effect either on the initial or on the recovery heat production of the isolated sartorius muscle of the frog. Injection of insulin into the intact frog produces convulsions which are relieved by glucose administration. J. P.

Studies on Carbohydrate Metabolism. II. On the Preparation of an Anti-diabetic Hormone from Yeast. I. H. B. HUTCHINSON, W. SMITH, and L. B. WINTER (*Biochem. J.*, 1923, **17**, 683—692).—A glucokinetic substance with physiological reactions closely resembling those of insulin may be extracted from yeast by methods similar to those used for preparing the pancreatic hormone. The lowering of blood-sugar may be followed by con-

vulsions which are relieved by glucose injections. Various yeasts give very variable results, and only in the case of active yeasts does the activity increase on culturing. J. P.

Studies on Carbohydrate Metabolism. III. On the Formation of an Anti-diabetic Hormone by the Action of a Bacillus. (Preliminary Communication.) H. B. Hutchinson, W. Smith, and L. B. Winter (*Biochem. J.*, 1923, **17**, 764—767).—Injection into rabbits of an extract of the medium in which cultures of a coliform bacillus from yeast had been grown, produced hypoglycæmia and convulsions which were relieved by glucose administration. J. P.

The Transformation of Creatine into Creatinine. A. Hahn and L. Schäfer (*Z. Biol.*, 1924, **80**, 195—210).—A series of experiments on rabbits and on human beings shows that neither oral administration nor subcutaneous injection of creatine causes an increased output of creatinine. Of the creatine administered, a variable proportion appears in the urine; the fate of the remainder is unknown. The transformation of creatine into creatinine is a function of the muscles, and depends on the physico-chemical conditions there obtaining (probably the most important being the hydrogen-ion concentration), and not on the action of an enzyme. C. R. H.

The Fate of Indolepropionic Acid in the Animal Organism. F. W. Ward (*Biochem. J.*, 1923, **17**, 907—915).—Indolepropionic acid was prepared by the anaërobic action of a mixed culture of *Bacillus coli*, *B. chauvei*, *B. sporogenes*, and *B. œdemaciens* on tryptophan (cf. Hopkins and Cole, A., 1903, i, 590). Intravenous injection of indolepropionic acid gives rise to a keto or enol form of a 2-hydroxyindole compound. Indole-ethyl alcohol is oxidised to indole-acetic acid, whilst indolecarboxylic acid is excreted unchanged as a conjugated compound, and is therefore not an intermediate step in the oxidation of indolepropionic acid. J. P.

Experiments with Two Methods for the Study of Vitamin-*B*. H. C. Sherman and Harriet Edgeworth (*J. Amer. Chem. Soc.*, 1923, **45**, 2712—2718).—The importance of vitamin-*B* as a factor in food values makes it desirable that quantitative methods of known precision be applied in all studies of the vitamin contents of different foods. The gravimetric yeast-growth method was employed, using the Williams medium, and dried skimmed milk was used as the source of the vitamin. The growth was continued for thirty hours at 18°, being then arrested by the addition of formaldehyde. Consistent results were obtained, the probable errors being of the order of 1% of the observed numerical values. The method is open to the objection that the increased growth measured may be due to the introduction of other substances favourable to yeast-growth. The rat-growth method was also used and gave quantitative results, the probable error being in this case 2—4% of the numerical values. F. G. P.

A Critical Investigation and an Application of the Rat-growth Method for the Study of Vitamin-*B*. H. C. SHERMAN and ADELAIDE SPOHN (*J. Amer. Chem. Soc.*, 1923, **45**, 2719—2728).—The rats used were fed on basal diets designed to be devoid of vitamin-*B*, and to contain all the other essential food factors in as nearly as possible the optimum proportions. Variations in the basal diets were made, fixed amounts of milk being used as sources of vitamin. It appears to be established from the results obtained that all increases of growth resulting from the addition of the milk to the basal diets used may be attributed to the vitamin-*B* thus furnished. There is no evidence of any measurable diminution of vitamin-*B* in milk powder heated dry at 100°, with free access of air. Probably about one-fourth of the vitamin is destroyed when the milk is heated in the fluid state for six hours at 100°.

F. G. P.

A Quantitative Study of the Destruction of Vitamin-*B* by Heat. H. C. SHERMAN and M. R. GROSE (*J. Amer. Chem. Soc.*, 1923, **45**, 2728—2738).—The juice of canned tomatoes was used as a source of vitamin-*B* in this investigation, and the effect of heating at 10° intervals over the range of 100—130° has been examined, using the rat-growth method (see preceding abstract) as a measure of the vitamin content. At 100°, in a slightly acid medium, there is an appreciable destruction of the vitamin, and the results obtained at different temperatures show that the temperature coefficient of the destructive process is distinctly lower than that of most chemical reactions, resembling, in this respect, that of vitamin-*C*. It is therefore improbable that the vitamin is an unstable protein, and inappropriate to group it with enzymes, since typical enzymes have shown rates of destruction by heat with high temperature coefficients up to the point at which the enzymic activity was entirely destroyed. F. G. P.

A Preliminary Note on the Destruction of Vitamin-*B* by Age. G. M. FINDLAY (*Biochem. J.*, 1923, **17**, 887—890).—Indian lentils and peas which had been kept for thirty-eight years and had lost their power of germination showed, when fed to rats, a slight loss of vitamin-*B* in comparison with recent samples of these seeds.

J. P.

The Alleged Specific Colour Reaction for the Antiscorbutic Factor. H. D. KAY and S. S. ZILVA (*Biochem. J.*, 1923, **17**, 872—874).—The blue colour given by the Bezssonoff reagent (*Bull. Soc. Chim. biol.*, 1922, **4**, 83) with certain preparations of the anti-scorbutic vitamin is not specific. The constituent responsible for the coloration is, like the vitamin, destroyed by oxidation.

J. P.

Contributions towards the Study of the Lipoids of the Human Brain. F. POPESCU (*Bul. Soc. Chim. România*, 1923, **5**, 83—92).—The author describes in detail the isolation of the lipoids present in the human brain, and extends the general methods for the determination of lipoids in blood (Grimbert and Laudet, A., 1913,

ii, 164) to this case. A new method for the desiccation of the brain by means of freezing is described. After complete freezing, the brain is maintained at 40° for half an hour and the soft paste so obtained dried rapidly and completely in a vacuum. Extraction of the dried powder with acetone removes cholesterol, fats, and the phosphatides. The cholesterol separates from the hot extract on cooling, and is removed by filtration. The whole of the cholesterol present in the brain is found to exist in the free state and not combined with oleic acid. From the residue, a new *lipoid*, of the phosphatide group, having the composition C = 67·02%, H=9·93%, N=2·50%, P=0·534%, was isolated. This is soluble in alcohol and acetone, insoluble in cold ether, is precipitated by cadmium chloride, and gives no reaction with nitric or sulphuric acid. The solution of the lipoids remaining is precipitated with lead acetate, and yields mainly lecithin and a small quantity of kephalin. The residue from the acetone extraction is extracted with light petroleum; addition of alcohol to the concentrated extract precipitates kephalin (7—8%), and the alcoholic solution contains lecithin (5·5%).

The residue insoluble in acetone and light petroleum is finally extracted with alcohol, and this extract yields the substances contained in the grey matter (protagon), sphingomyelin (containing phosphorus) and phrenosin, and kerasin (phosphorus-free).

The determination of the lipoids present in a tubercular brain shows that the quantity of cholesterol is larger, and the quantity of other lipoids smaller, than in the normal brain.

For details of the separation and determination, the original paper must be consulted. J. W. B.

Gradual Decomposition of Proteins. Partial Hydrolysis of Keratin (Hog Bristles). E. Abderhalden and E. Komm.—(See p. 343.)

Auto-histo-radiographic Method for the Detection in Organs of Injected Polonium. A. Lacassagne and (Mme.) J. S. Lattès (*Compt. rend.*, 1924, **178**, 488—490).—The authors have made use of the α-ray emission of polonium, and its relatively long period of disintegration of 140 days, to obtain auto-radiograms of organs capable of retaining it. A rabbit was injected with polonium salts and killed after six days. Thin sections of the principal organs were made and placed on the sensitive surface of a photographic plate. After several days' exposure, records were obtained of the distribution of polonium. Retention by the various organs was very unequal, being greatest in the organs of elimination.

A. B. H.

Researches on Cellular Disintegration. A. Nodon (*Compt. rend.*, 1924, **178**, 486—487).—It is shown that living organisms, vegetable and animal, exhibit radioactivity, which appears to be a function of the degree of vitality of the organism. The radioactivity varied with the nature of the organism, and was increased by sunlight. The conclusion is drawn that both the disintegration

of radium and that of the living cell have their origin in exterior ultra-radiations, also that the atoms constituting the living material must acquire special properties, which allow them to disintegrate in a manner similar to those of the radioactive elements.

A. B. H.

[**Cellular Disintegration.**] D. BERTHELOT (*Compt. rend.*, 1924, **178**, 487).—The author observed in 1909 and 1910 phenomena similar to those observed by Nodon (preceding abstract). These he found to be due solely to changes of humidity. A. B. H.

The Extraction of the Concretion Gland and Nephridium of *Cyclostoma elegans*. P. QUAST (*Z. Biol.*, 1924, **80**, 211—222).—A qualitative analysis of the concretion gland indicated the presence of silicates among the inorganic constituents and of uric acid, xanthine, hypoxanthine, and adenine among the organic ones. In the nephridium were found creatinine and allantoin.

C. R. H.

On the Participation of a Peroxidase in the Appearance of the Pigment in *Drosophila melanogaster*, Loew. DE LUNA (*Compt. rend.*, 1924, **178**, 525—527).—It is shown that a peroxydase takes part in the pigmentation of *Drosophila*. The peroxydase has the same distribution as the pigment. The appearance of the pigment is a function of temperature if the quantities of oxygen and peroxydase are constant; anæsthetics retard pigmentation.

A. B. H.

The Extractives of *Eledone moschata*. D. ACKERMANN, F. HOLTZ, and F. KUTSCHER (*Z. Biol.*, 1924, **80**, 155—162).—From this organism the authors have isolated betaine, taurine, lactic acid, and in addition two new bases which are designated *eledonine* ($C_{14}H_{30}O_3N_2$) and *homoeledonine* ($C_{15}H_{32}O_3N_2$). They both give chloroaurates melting indefinitely at 225—235°. The formula previously given to crangonine (A., 1908, ii, 53) is revised and now becomes $C_{13}H_{28}O_3N_2$, so that these three bases would appear to be members of an homologous series. C. R. H.

The Extractives of *Holothuria tubulosa*. D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, **80**, 163—170).—In addition to betaine, adenine, and lactic acid, there was obtained from the lysine fraction a *chloroaurate* (m. p. 134°) of a base isomeric with homoeledonine (see preceding abstract). This substance on hydrolysis with hydrochloric acid gives betaine, and has therefore been named betainogen. C. R. H.

The Extractives of *Mytilus edulis*. D. ACKERMANN (*Z. Biol.*, 1924, **80**, 193—194).—Adenine was obtained in the purine fraction, and in the filtrate from the phosphotungstic acid precipitation was found the cyclose mytilitol (A., 1921, i, 764). C. R. H.

Proteins of Milk-serum. Their Separation by the Acetone Method. M. PIETTRE (*Compt. rend.*, 1924, **178**, 333—335).—The milk is coagulated rapidly by shaking at 35° and adding rennet,

drop by drop, until casein begins to separate in a flocculent condition, after which the serum is filtered off by suction. It is rendered feebly acid with hydrochloric acid, extracted with ether, and the residual liquid precipitated by means of acetone and filtered. The precipitate is digested with water, and $N/10$-hydrochloric acid added in sufficient quantity to precipitate the lactoglobulin, which is then collected (using a centrifuge) and found to have $[\alpha]_D$ $-31°$ 12′ in aqueous sodium hydroxide solution. The clear filtrate on precipitating, *e.g.*, with alcohol, affords the pure lactalbumin, with $[\alpha]_D$ $-41{\cdot}23°$. Milk contains, on the average, 2·3 g. of globulin and 3·2 g. of albumin per l. E. E. T.

Observations on certain Reducing and Oxidising Reactions of Milk. P. Haas and T. G. Hill (*Biochem. J.*, 1923, **17**, 671—682).—There is present in milk an oxygen acceptor capable of reducing sodium nitrate to nitrite, to which the name "*atite*" is provisionally given, and also an oxygen donator bringing about the reverse conversion of nitrite to nitrate (cf. Bach, A., 1911, i, 759) which has been called "*itate*." Atite is precipitated with the milk proteins, and, although thermolabile, is not regarded as being an enzyme. Unlike atite, which is most active in the absence of oxygen, itate is active only in its presence, but in its thermolability and precipitation reactions it resembles the former. Both substances require an accelerator, aldehydes, notably acetaldehyde, being most active. Acetaldehyde in the presence of oxygen destroys both atite and itate. The diminution in the peroxydase reaction of milk is parallel to the rate of destruction of itate, and the possible identity of the last with peroxydase is considered. Atite is distinct from Schardinger's reductase. J. P.

The Protein Matter of Bile. J. F. Logan.—(See p. 341.)

The Occurrence of Amines in Urine. P. N. van Eck (*Pharm. Weekblad*, 1924, **61**, 65—73).—In testing samples of urine for blood, it was occasionally observed that a beautiful orange-red colour developed on addition of benzidine and glacial acetic acid, and before the addition of hydrogen peroxide. Out of 61 samples of urine, 25 gave positive results. Investigation failed to show that this was due to any specific malady or remedy. Negative tests were obtained with some twenty substances likely to be present in urine, and with the extracts obtained by shaking urine with the ordinary organic solvents. It was found, however, that the distillates from many urines gave the reaction, and contained alkylamines; the lower alkylamines were then examined, and all gave the reaction. By testing urine from healthy persons it was found that a positive result always followed a meal of pickled herrings, in which amines were identified, and that amines could be identified in the distillates from these urines, by the *iso*nitrile and nitroprusside reactions.

A collection of observations on the occurrence of alkylamines in animal and vegetable matter from various sources is given.

S. I. L.

Camphorylcarbamates and their Physiological Action. H. E. FIERZ-DAVID and W. MÜLLER.—(See i, 301.)

The Physiological Effect of Gossypol. P. MENAUL (*J. Agric. Res.*, 1923, **26**, 233—237).—The toxic effect of gossypol on rabbits was slow to appear if the substance was given with the food, but when it was injected directly into the blood-stream, the effects were apparent almost at once. It was found that gossypol prevents the normal oxygen-interchange in the blood, and also has a hæmolytic effect. Death is caused by a reduced oxygen-carrying power of the blood, which considerably increases the work of the respiratory and circulatory organs. This explained the condition of dead animals, viz., a passive hyperæmia and œdema of the lungs and some hydrothorax, which is directly due to the effect of gossypol and does not result from bacterial action. A. G. P.

Hypnotic Properties of Hydrobenzoin and of its Alkylated Homologues (Symmetrical Diarylglycols). Relations between Physiological Activity and Molecular Weight. M. TIFFENEAU and C. TORRES (*Compt. rend.*, 1924, **178**, 237—239).—The hypnotic effect, on the stickleback, of hydrobenzoin, and of its methyl, ethyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl derivatives has been measured (cf. A., 1923, i, 676). It is concluded that the hypnotic effect and molecular weight increase together. When, in a series (*e.g.*, in the present one, at the *iso*amyl member) the solubility limit is reached, the hypnotic effect then decreases as the molecular weight increases, unless biliary substances are added to promote absorption by the organism. E. E. T.

Constitution and Mode of Action of Biochemical Catalysts or Enzymes. Effects of Electrolysis on Enzymes of Pancreatic Juice and on the Amylase of Germinated Barley. F. MAIGNON (*Compt. rend.*, 1924, **178**, 420—423).—Preparations of the enzymes from the pancreatic juice of the cow, and of amylase from barley have been found to contain calcium, iron, and chlorine. On being electrolysed in aqueous solution, coagulation sets in near the anode, but not near the cathode. Finally, coagulation ceases, and the enzyme is found to be inactive, owing to removal of the inorganic constituents by electrolysis. The author concludes that the chlorine-ion is attached to the proteinic micellæ, the kations (Fe and Ca) being free in the liquid medium. In the case of hydrion, the latter is adsorbed on the external surface of the micellæ, this explaining (on ordinary adsorption theories) the great catalytic activity of that hydrion. E. E. T.

The Azine and Azonium Compounds of the Proteolytic Enzymes. I. H. R. MARSTON (*Biochem. J.*, 1923, **17**, 851—859).—Dyes of the azine group (eurhodines, safranines, indulines), but not their leuco-bases, quantitatively precipitate the proteolytic enzymes pepsin, trypsin, erepsin, and papain from their solutions. The enzyme is regarded as attaching itself to the azine nitrogen atom or atoms. Pepsin may be recovered in solution from the pepsin–azine precipitate by treatment with 0·5% hydrochloric acid and removal of the dye by extraction with amyl alcohol. It is

suggested that the proteolytic enzymes may become attached to proteins, preliminary to hydrolysing them, through the nitrogen atoms of diketopiperazine groupings, and the results are interpreted in favour of the view that such groupings are present in the protein molecule. J. P.

Further Studies on the Enzymic Degradation of Polypeptides Composed of Amino-acids not yet found among the Degradation Products of the Proteins. E. ABDERHALDEN and A. MOSCHINI (*Fermentforschung*, 1923, **7**, 176—178).—Yeast maceration juice degrades *d*-*n*-valyl-*l*-tyrosine but not *l*-*n*-valyl-*l*-tyrosine. In the former case, the formation of tyrosine and *d*-α-amino-*n*-valeric acid was demonstrated. The dipeptides were synthesised by combining *l*-tyrosine or its ester with *d*- or *l*-α-bromo-*n*-valeryl chloride. S. S. Z.

The Action of Enzyme Solutions on 3 : 5-Di-iodo-*l*-tyrosine and Glycyl-3 : 5-di-iodo-*l*-tyrosine. E. ABDERHALDEN and W. STIX (*Fermentforschung*, 1923, **7**, 179—182).—Yeast maceration juice effects a cleavage in glycyl-3 : 5-di-iodo-*l*-tyrosine. Extract of pancreas and of the mucous membrane of the stomach do the same, but more slowly. Thyroid extract and thyroid press-juice have no action on the compound. S. S. Z.

The Action of the Enzymes of the Gastro-intestinal Tract on Diketopiperazine. E. ABDERHALDEN and K. GOTO (*Fermentforschung*, 1923, **7**, 169—175).—It is concluded that neither trypsin nor pepsin has an appreciable hydrolytic action on *d*-alanylglycine anhydride, and that the hydrolysis which is effected by alkaline or acid solutions of these enzymes is due to that alkalinity or acidity. The anhydride was obtained by hydrolysing silk resides. S. S. Z.

Urease. II. The Mechanism of the Zymolysis of Urea. W. R. FEARON (*Biochem. J.*, 1923, **17**, 800—812).—Using the method described by the author (A., 1923, i, 497), it is shown that cyanic acid and ammonia, but not carbamic acid, are intermediate products of the zymolysis of urea (cf. Mack and Villars, A., 1923, i, 405). Soja urease, which carries a negative electric charge, adsorbs urea from alcoholic solution and ammonia from aqueous solution. It is concluded that urease adsorbs its substrate, and that the adsorbed urea is then decomposed into ammonia and cyanic acid. The former is readsorbed as such by the enzyme and the latter is hydrolysed by the solvent water. The enzyme is again liberated by combination of the adsorbed ammonia with ammonium hydrogen carbonate and is free to adsorb more urea. The cyclic process continues until arrested by accumulation of ammonium carbonate or by exhaustion of the substrate. J. P.

Studies on Enzyme Action. The Relationship between the Chemical Structure of certain Compounds and their Effect upon the Activity of Urease. E. W. ROCKWOOD and W. J. HUSA (*J. Amer. Chem. Soc.*, 1923, **45**, 2678—2689).—The effect of various compounds on the activity of urease obtained from jack-bean meal has been studied, and the following results have been obtained,

Certain compounds exert a promoter effect on the catalytic activity of the urease, others have an inhibitory action. These effects are independent of changes in hydrogen-ion concentration. The promoter effect is related to the presence of both amino and carboxyl groups. Compounds containing only one of these groups were not promoters. The promoter action seems to be a function of the distance between the groups, all the α-amino-acids used being marked promoters, β-amino-acids having a slight effect, and γ-amino-acids none. With the aminobenzoic acids, the order of decreasing effect is ortho, meta, para. A second amino or carboxyl group in an α-amino-acid increases the promoter action. α-Amino-acids of the heterocyclic nitrogen compounds have a slightly greater effect than simple α-amino-acids. Ammonium chloride, guanidine sulphate, creatine, and creatinine have no promoter effect. Enzymes appear to be of a protein nature or to occur associated with protein, and when the protein is removed from the enzyme solution, the activity is lost. The experiments which show the promoter action of α-amino-acids and peptones indicate that the protein part of enzyme preparations is an important factor in the action of the enzyme. The results obtained also tend to disprove the hypothesis that the promoter effect is due chiefly to prevention of decomposition of the enzyme. F. G. P.

Experiments Demonstrating the Existence of Specific Cytolysins for the Various Organs of the Animal Organism. A. Zerkowitz (*Fermentforschung*, 1923, **7**, 223—228).—It is claimed that some of the experiments carried out with the blood sera of normal and castrated rabbits, and the testicles and other organs of these animals, confirm the author's hypothesis of the existence of specific cytolysins. S. S. Z.

Carbohydrate and Fat Metabolism in Yeast. I. S. Maclean and D. Hoffert (*Biochem. J.*, 1923, **17**, 720—741).—Yeast incubated in oxygenated water shows a diminished carbohydrate content and an increase in fat. Propyl, butyl, and *iso*amyl alcohols inhibit this conversion, whilst the sodium salts of formic, propionic, and butyric acids, glycol, glycerol, and acetone, in 0·1*M*-solution, behave like water. Incubation in 0·5% solutions of ethyl alcohol, or of the sodium salts of acetic, lactic, and pyruvic acids gives the same results as 0·5% solutions of dextrose; in the first two cases increase of the total carbohydrate of the yeast-cell is observed. In the presence of dextrose, lævulose, and sucrose the yeast-cell stores both carbohydrate and fat. Maltose is exceptional in producing a greater carbohydrate and lesser fat storage than the other sugars investigated. It is suggested that maltose is assimilated as such by the yeast-cell. Continuous oxygenation during incubation greatly increases the amount of fat produced, but has little or no effect on the carbohydrate. In oxygenated solutions, added phosphate reduces the amount of carbohydrate stored and increases the fat formation. Phosphate is taken up by the cell in proportion to the sugar concentration of the solution; more phosphate is taken up from oxygenated than from non-oxygenated solutions. It is

suggested that the formation of hexose phosphate is the first stage in the conversion of carbohydrate into fat. J. P.

Irregularities of the Lactic Fermentation in Presence of certain Antiseptics. A. LUMIÈRE (*Compt. rend.*, 1924, **178**, 258—260).—It is shown that the supposed irregularity observed by Richet (*ibid.*, 1923, **177**, 1262) in connexion with the antiseptic action of mercuric chloride is due to the use, by this author, of inocula from non-uniform bacterial suspensions. If the latter are well shaken, in order to break up large aggregates, perfectly uniform results are obtained with antiseptics. E. E. T.

Production of β-Hydroxybutyric Acid by Microbial Processes. M. LEMOIGNE (*Compt. rend.*, 1924, **178**, 253—256; cf. A., 1923, i, 881).—The alcoholic extract of fresh cultures of *Bacillus M.* gives, on evaporation and distillation of the residue, α-crotonic acid. β-Hydroxybutyric acid is therefore a normal physiological product of the bacillus, and is formed from intracellular reserve material. E. E. T.

Variations in Hydrogen-ion Concentration under the Influence of the Assimilation of Nitrates by *Aspergillus repens*, De Bary. BACH (*Compt. rend.*, 1924, **178**, 520—522).—When *Aspergillus repens*, De Bary, is allowed to grow in a suitable medium containing nitrates and for which p_H has an initial value between 3·6 and 8·4, the hydrogen-ion concentration after ten days approximates to the value $p_H = 6$. The addition of potassium phosphate reduces the rate of the change, but does not alter its sense. A. B. H.

The Accumulation and Formation of Urea in Mushrooms. N. N. IVANOV (*Biochem. Z.*, 1923, **143**, 62—74).—The urea content and nitrogen distribution in mushrooms, artificially cultivated in manure, has been estimated at various stages of growth. The dried fungi may contain up to 13% of urea. The amount of urea increases during the ripening process until spore formation begins, autolysis of the proteins and chitin leading to an increase in the amino compounds, which are then converted to urea. By treatment with chloroform, the formation of urea may be inhibited. The high urea content is ascribed to the artificial culture in the nitrogen-rich medium. A close analogy is drawn between the formation of urea and asparagine (cf. also A., 1923, i, 428, 520). J. P.

The Migration of Inulin in the Grafts of Composites. H. COLIN and R. FRANQUET (*Compt. rend.*, 1924, **178**, 518—520).—It is shown that when a branch of a plant containing inulin is grafted on a subject which does not normally contain this substance, the latter migrates into the subject, but undergoes hydrolysis to lævulose. It is sometimes possible, however, to detect the inulin in the immediate vicinity of the graft. The optical rotations of the sugars above and below the graft are frequently in opposite direction. A. B. H.

The Acidity of Maize and its Relation to Vegetative Vigour. A. M. HURD (*J. Agric. Res.*, 1923, **25**, 457—468).—Measurements

of the hydrogen-ion concentration and titratable acidity of the expressed juice of maize plants, showed these two factors to vary inversely as the vigour of the plant. Alterations in sap density did not account for variations in acidity, with the exception of a few cases where particularly high values were obtained. The concentration of titratable acid in the leaf-juice was always greater than in the stalk, whatever the state of vigour of the plant. In vigorous plants, the p_H values of the leaf juices were greater than those of the stalk juices. This relationship was reversed in the case of weakly, stunted plants. The density of the juice of the leaves was greater than that of the stalks, whether the plant was vigorous or otherwise. Variations in the acidity of plants of the same strain but in a different environment were considerably greater than those of different varieties under similar conditions of growth and vigour.

A. G. P.

On the Significance of the Ash Content of certain Marine Algæ. P. Haas and B. Russell-Wells (*Biochem. J.*, 1923, **17**, 696—706).—From a comparison of the sulphate content of the hydrolysed aqueous extracts of certain marine algæ (*Rhodophyceæ* and *Phæophyceæ*) with the sulphate content observed after incineration, it is found that the former is greater than the latter and frequently in the ratio 2 : 1. This is ascribed to the presence of a complex calcium organic sulphate of the type $R<^{O\cdot SO_2\cdot O}_{O\cdot SO_2\cdot O}>Ca$, in which the calcium, but not the sulphate, is freely ionised. These colloidal complexes have a measurable conductivity and osmotic properties to which considerable importance is attached (cf. Harwood, T., 1923, **123**, 2254).

J. P.

On the Determinable Iodine of *Laminaria flexicaulis*. P. Freundler (*Compt. rend.*, 1924, **178**, 515—517).—The iodine content of perfectly fresh *Laminaria flexicaulis* has been determined by three methods. The author concludes that the alga contains, in addition to its normal iodide content, a fairly constant quantity of a substance of unknown composition which is transformed into iodide on the death of the organism.

A. B. H.

Quantitative Diurnal Variation of Starch in Green Plant Leaves. P. P. Stanescu (*Compt. rend.*, 1924, **178**, 117—119).—The starch-content of green leaves has been determined hourly or half-hourly, successive strips being cut from the same leaf at these intervals, and extracted with boiling water and alcohol. At the end of the day, the leaf is reassembled, and developed by immersion in iodine–iodide solution. The variation of starch-content throughout the day is then clearly seen. With most leaves (particularly from March to July) a single daily starch maximum is observed (*Robinia pseudacacia*, etc.). In August and September, two maxima are often observed. Several maxima are rarely found (*Rhus typhina* showing five). With *Chelidonium majus* and *Atriplex patula*, maxima and minima succeed each other rhythmically, whilst with *Urtica dioica* starch suddenly appears and as suddenly disappears again.

E. E. T.

Galuteolin, a New Glucoside from *Galega officinalis*. G. BARGER and F. D. WHITE (*Biochem. J.*, 1923, **17**, 836—838).—From the seeds of *Galega officinalis* a glucoside, $C_{21}H_{20}O_{11},3H_2O$, to which the name *galuteolin* is given, has been isolated. It contains no methoxyl groups. On hydrolysis, it yields dextrose and an insoluble yellow colouring matter decomposing at 290—300°, of the composition $C_{15}H_{10}O_6$, identified as luteolin, which, when boiled with acetic anhydride containing a trace of sulphuric acid or pyridine, forms a tetra-acetyl compound, $C_{15}H_6O_6(C_2H_3O)_4$, long, colourless needles, m. p. 221—223°. Luteolin occurs as such in the seeds of *Galega officinalis*. The temperatures at which hydroxyflavones such as luteolin sublime in a high vacuum are characteristic. J. P.

Localisation of the Cyanogenetic Glucosides in *Prunus occidentalis* and *P. myrtifolia*. E. MAMELI-CALVINO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 423—430).—By means of Treub's Prussian blue reaction the author has established the localisation of a cyanogenetic glucoside in the bark and leaves of *Prunus occidentalis* and *P. myrtifolia*. Peche's mercurous nitrate method is unsuitable for this purpose, since the reagent may be reduced by the action of cellular constituents which yield no hydrocyanic acid. Microchemical investigation fails to reveal the presence of alkaloids in the bark or leaves of these two species. T. H. P.

A Labile Form of Protein and its Relation to Living Protoplasm. II. O. LOEW (*Biochem. Z.*, 1923, **143**, 156—160).—The occurrence is described, in various vegetable cells, of rounded, highly refractive protein droplets resembling the "caffeine proteosomes" previously discovered by the author (A., 1915, i, 1079). These are coagulated by the vapour of ether and chloroform, and combine with bases to form insoluble stable complexes. They also combine readily with water and are made insoluble by neutral salt solutions and by hydrocyanic acid. The reactivity of these droplets is discussed in relation to protoplasmic activity. J. P.

Proteins of Wheat Bran. I. Isolation and Elementary Analyses of a Globulin, Albumin, and Prolamine. D. B. JONES and C. E. F. GERSDORFF.—(See this vol., i, 342.)

Detection and Distribution of Phytosterols in Latex. G. KLEIN and K. PIRSCHLE (*Biochem. Z.*, 1923, **143**, 457—472).—An improvement is effected in the method available for the extraction of phytosterols from dried plant residues, by shaking the extract dissolved in light petroleum with 50% aqueous sodium hydroxide, whereby the impurities, which render recrystallisation difficult, are hydrolysed and may be subsequently washed out with aqueous sodium carbonate and distilled water. Crystallisation of the phytosterols then proceeds readily. Euphorbone has been obtained in this way, not only from the *Euphorbiaceæ*, but also from many other latex-forming plants, and its nature as a phytosterol has been established by the digitonin test (cf. Windaus, A., 1910, ii, 462).

The presence of 0·1 to 2·0% of phytosterol in latex is regarded as characteristic. A *bromo-* (m. p. 83°) and a *nitro*-derivative of euphorbone are described; a benzoyl derivative was not obtained (cf. Emmerling, A., 1908, i, 438). The physiological significance of phytosterols is discussed. J. P.

A Crystalline Metabolic Product from *Sparassis ramosa*. R. Falck (*Ber.*, 1923, **56**, [*B*], 2555—2556).—Remarkable growth of crystals is observed in pure cultures of *Sparassis ramosa* both in the substrate and on the surface. On the latter they are formed as long needles, in the former as small, rounded crystalline aggregates. The substance possesses the power of protecting the cultures from impurities in a remarkable manner. It can be isolated almost quantitatively by distillation of the substrate with steam. Its constitution has been elucidated by Wedekind and Fleischer (this vol., i, 174), by whom it has been designated "sparassol." H. W.

The Effect of Physiologically Acid and Alkaline Nitrogenous Fertilisers. F. Münter (*Z. Pflanz. Düng.*, 1923, **A**, **2**, 497—516).—The results of pot trials of the effect of various fertilisers on the yield of wheat and linseed are reported. They confirm the conclusions of earlier experiments. Physiologically acid nitrogenous fertilisers such as ammonium sulphate increase the availability of phosphorus in sandy soils so long as the soil reaction remains alkaline. Where a soil contains very small quantities of calcium carbonate, ammonium sulphate may depress the yield. The production of "alkali" in the soil as a result of heavy dressings of sodium nitrate depresses the availability of phosphorus and crop yield. Flax is more sensitive to alkalinity than is wheat. G. W. R.

Physiological Function of Iodine in the Sugar-beet. J. Stoklasa (*Compt. rend.*, 1924, **178**, 120—122).—Iodine (present as potassium iodide), although inimical to many plants, is absorbed by the leaves and roots of the sugar-beet, the weight of the whole plant and the percentage sucrose content increasing as a result. The moderate use (about 2 lb. per acre) of potassium iodide as a practical fertiliser in sugar-beet growing is therefore to be recommended, this applying even in the second year. A too free use (*e.g.*, 4 lb. per acre) of iodide, however, diminishes the growth and sucrose content, some arabinose appearing in the roots. E. E. T.

Lysimetric Studies. Soil and Subsoil in Calcium–Magnesium Interchange. W. H. MacIntire, W. M. Shaw, and J. B. Young (*Soil Sci.*, 1923, **16**, 321—341; cf. A., 1923, i, 1168).—Further data are given in connexion with lysimetric studies on soils treated with different compounds of calcium and magnesium. It is shown that the general effect of calcium dressings is to depress the outgo of magnesium from the soil and to increase the outgo from the subsoil. Magnesium dressings have a similar effect on the outgo of calcium from soil and subsoil. G. W. R.